THE CRYSTAL STRUCTURES OF SOME o-HALOGENO-AROYL COMPOUNDS AND OF A PALMARIN DERIVATIVE

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by

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SUMMARY

This thesis is divided mainly into three sections (see outline): the first section is a brief description of the theory and methods of x-ray crystal structure analysis, the second section describes the crystal structures of four o-halogeno-aroyl compounds and the third one includes the structure of a palmarin derivative. There are two appendices in the thesis. The first one is a brief account of the unsuccessful attempt to solve the structure of phorbol and the second being the improvement of the existing apparatus for Nonius Weissenberg cameras to collect photographic data at low temperature.

Section I is divided under nine broad headings giving a short review of the crystal geometry, theory and methods of x-ray crystal structure analysis, refinement of atomic parameters and evaluation of the accuracy of the final results.

There are five chapters in Section II. The crystal structures of o-chlorobenzoylacetylene and o-bromobenzoylacetylene are described in the Chapters 1 and 2 respectively. Intramolecular overcrowding and intermolecular ethynyl hydrogen bonds are present

in both the structures. Chapter 3 contains the structure of o-fluorobenzoic acid and that of 2-chloro-1, 8-phthaloylnaphthalene is described in Chapter 4. The detailed findings of the characteristic features of the conformation, intermolecular hydrogen bonding and intramolecular overcrowding in different o-halogeno-aroyl compounds are discussed in Chapter 5.

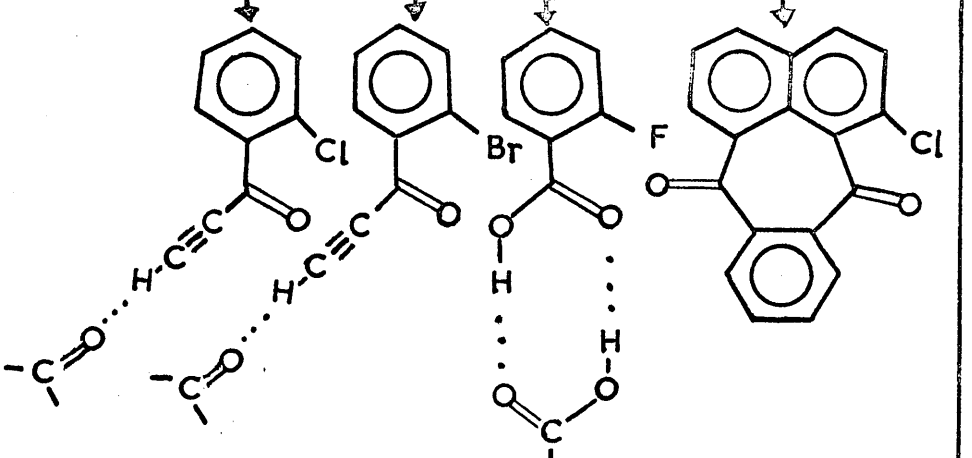
The crystal structure analysis of p-bromophenacyl derivative of palmarin is described in Section III. The confirmation of the β-epoxide configuration of the palmarin derivative has decided the configuration of the epoxide in a series of Colombo root bitter principleshaving composition $C_{20}H_{22}O_7$ (palmarin, jateorin and chasmanthin). The structure analysis has also revealed the special distortion of the molecule.

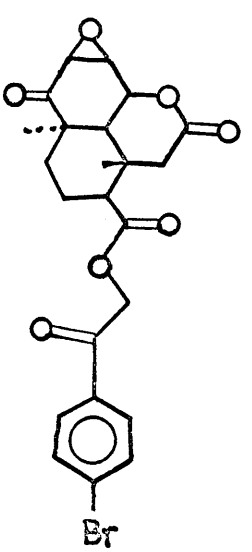
A brief account of the unfruitful attempt to solve the structure of phorbol, a natural product, using three different solvate derivatives is given in Appendix A. The short description of the arrangement for taking photographs in the cold nitrogen atmosphere can be seen in Appendix B.

OUTLINE

THE CRYSTAL STRUCTURES OF SOME o-HALOGENO-AROYL COMPOUNDS AND OF A PALMARIN DERIVATIVE

- SECTION I — SOME METHODS OF X-RAY CRYSTAL STRUCTURE ANALYSIS
- SECTION II — o-HALOGENO-AROYL COMPOUNDS
  - CHAPT. 1
  - CHAPT. 2
  - CHAPT. 3
  - CHAPT. 4
  - CHAPT. 5
- SECTION III — *p*-BROMO-PHENACYL DERIVATIVE OF PALMARIN
- APPENDICES
  - A — PHORBOL
  - B — LOW TEMP. WORK





GENERAL DISCUSSION

CONTENTS

Chapter 2

(o-Bromobenzoylacetylene)

Chapter 3

(o-Fluorobenzoic acid)

Chapter 4

(2-Chloro-1, 8-phthaloylnaphthalene)

Chapter 5

(General discussion)

SECTION III

CRYSTAL STRUCTURE OF p-BROMOPHENACYL DERIVATIVE OF PALMARIN

APPENDICES

SECTION I

SOME METHODS OF X-RAY CRYSTAL STRUCTURE ANALYSIS

1.1 INTRODUCTION

The early crystallography dates back to the beginning of the seventeenth century, when Johannes Kepler, the great astronomer, being inspired by the beautiful regular shaped snowflakes conceived the idea that this regularity might be inherent in some minute fundamental identical units. In 1890, E.S. Fedorov and A.Schoenflies derived the 230 space groups. Further progress was awaiting the discovery of x-rays by Wilhelm Conrad Röntgen (in 1895). Bragg (1913) gave the physical concept of x-ray diffraction discovered by von Laue (1912), and had opened the door to the new horizon of x-ray crystallography.

The fundamental object of x-ray crystal structure analysis is to study the diffraction pattern of an x-ray beam scattered by the cloud of electrons surrounding the atomic nuclei, and to infer the geometry of the electron density distribution. Because of the enormous calculations involved and the limited knowledge of the techniques for determining the phases of the diffracted patterns, it was once a difficult task to solve even a small simple structure; with the application of the electronic computer and through the advent of new methods of overcoming the crystallographic "phase problem" more and more complex structures are being solved.

1.2 GEOMETRY OF X-RAY DIFFRACTION

1.2.1 Crystal lattice

Crystals are composed of identical groups of atoms arranged in a regular manner in three dimensions. An array of such identical points is called a crystal lattice.

1.2.2 Laue equations

If we assume that each lattice point is the site of an electron, then its position can be expressed in terms of a vector, $\underline{R}$, as

$$\underline{R} = m\underline{a} + n\underline{b} + p\underline{c} \qquad (1)$$

where m, n, p are integers and $\underline{a}$, $\underline{b}$, $\underline{c}$ are the primitive translations of the lattice.

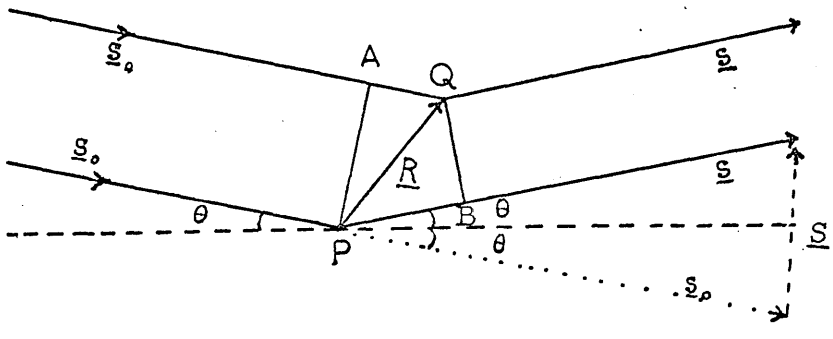


FIG. 1.1

Let a parallel beam of x-rays of wavelength λ, falling in the direction of the vector $\underline{s}_o$ on two lattice points P and Q, separated by a vector distance, $\underline{R}$, be diffracted in a way parallel to the vector $\underline{s}$ (Fig. 1.1). If AP and BQ indicate the directions of incident and diffracted wave fronts respectively and the magnitude of both the vectors, $\underline{s}$ and $\underline{s}_o$, be $1/\lambda$, the path difference between the incident and diffracted beam will be

$$\begin{aligned} & PB - AQ \\ &= \lambda(\underline{R}.\underline{s} - \underline{R}.\underline{s}_o) \\ &= \lambda\, \underline{R}.(\underline{s} - \underline{s}_o) \\ &= \lambda\, \underline{R}.\underline{S} \qquad (2) \end{aligned}$$

where $\underline{S} = \underline{s} - \underline{s}_o$

In order to have phase agreement in the diffraction $\underline{R}.\underline{S}$ must be an integer. Hence putting the value of $\underline{R}$ from eqn. (1) in eqn. (2)

$$(m\underline{a} + n\underline{b} + p\underline{c}).\underline{S} = \text{Integer}$$

Since m, n, p are integers,

$$\left.\begin{aligned} \underline{a}.\underline{S} &= \text{Integer} \\ \underline{b}.\underline{S} &= \text{Integer} \\ \underline{c}.\underline{S} &= \text{Integer} \end{aligned}\right\} \qquad (3)$$

let h, k and ℓ be the values of these integers; therefore eqns. (3) can be re-written as

$$\left.\begin{aligned} \underline{a}.\underline{S} &= h \\ \underline{b}.\underline{S} &= k \\ \underline{c}.\underline{S} &= \ell \end{aligned}\right\} \qquad (4)$$

These are called the Laue equations.

1.2.3 Bragg equation

The Laue equations (4) can be written in the form

$$\underline{a} / h \,.\, \underline{S} = \underline{b} / k \,.\, \underline{S} = \underline{c} / \ell \,.\, \underline{S} = 1 \qquad (5)$$

$$\text{i.e. } (\underline{a} / h - \underline{b} / k) \,.\, \underline{S} = 0 \qquad (6)$$

It means that the vector $\underline{S}$ is perpendicular to $(\underline{a} / h - \underline{b} / k)$.

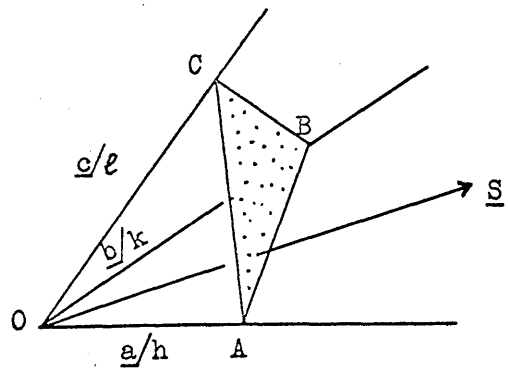


FIG. 1.2

Similarly it can be shown that $\underline{S}$ is also perpendicular to $\frac{\underline{b}}{k} - \frac{\underline{c}}{\ell}$ i.e. $\underline{S}$ is perpendicular to the plane ABC (Fig. 1.2), which has intercepts $\underline{a}/h$, $\underline{b}/k$, and $\underline{c}/\ell$ on the unit cell axes; i.e. $\underline{S}$ is perpendicular to the plane having Miller indices h, k, ℓ. This is the major contribution of Bragg (1913) to identify h, k, ℓ of the Laue equations with Miller indices.

The distance, d, from the origin, O, to the plane ABC (Fig. 1.2) is the projection of $\underline{a}/h$, $\underline{b}/k$ and $\underline{c}/\ell$ on the unit vector in the direction $\underline{S}$.

$$\text{i.e.} \quad d = \frac{\underline{a}/h \,.\, \underline{S}}{|\underline{S}|}$$

From eqn. (5)

$$\underline{a}/h \,.\, \underline{S} = 1$$

$$\therefore \quad |\underline{S}| = \frac{1}{d} \tag{7}$$

From Fig. 1.1 it can be shown that

$$|\underline{S}| = \frac{2 \sin\theta}{\lambda} \tag{8}$$

Therefore from (7) and (8)

$$\lambda = 2d \sin\theta \tag{9}$$

This is the Bragg equation which allows the x-ray

diffraction by a crystal to be considered in terms of the simple concept of optical diffraction (Bragg, 1913).

1.2.4 Reciprocal lattice

Eqn. (5) shows that for a particular value of h the projection of $\underline{S}$ on $\underline{a}$ is constant i.e. the end of the vector $\underline{S}$ lies on a plane perpendicular to $\underline{a}$; corresponding to different values of h (= 0, 1, 2 etc.) an array of such planes of constant spacing is set up. In a similar manner, corresponding to the increasing values of k and ℓ there will be other two groups of planes. The intersections of these three sets of planes represent the end points of the vectors which satisfy the three Laue equations (4) simultaneously, and give the required solutions. The points of intersections of these sets of planes form an array, called the reciprocal lattice. The unit cell of this lattice is defined by the three vectors a^*, b^* and c^*, which can be represented as

$$a^* = \frac{\underline{b} \times \underline{c}}{V} \qquad (10)$$

$$b^* = \frac{\underline{c} \times \underline{a}}{V} \tag{11}$$

$$c^* = \frac{\underline{a} \times \underline{b}}{V} \tag{12}$$

where $V = \underline{a} . \underline{b} \times \underline{c} = \underline{b} . \underline{c} \times \underline{a} = \underline{c} . \underline{a} \times \underline{b}$ = Volume of the unit cell of space lattice.

1.3 FACTORS AFFECTING INTENSITY

1.3.1 Atomic scattering factor

The maximum scattering power (f) of an atom is defined as the total scattering ability of all its electrons and is equal to Z, the atomic number (see eqn. 32). f is also a function of $\sin \theta / \lambda$, where θ is the scattering angle and λ is the wave-length of the x-rays. Due to the uncertainty of the knowledge of the exact density functions of all the atoms (except the hydrogen atom), scattering factors calculated by different methods for various atoms cannot be expected to be absolutely accurate; the extent of the accuracy depends upon the reliability of the electron density functions

employed. A list of the scattering factors for various chemical atoms and an appropriate concise bibliography can be seen in Int. Tables, Vol. III (1962).

A further complication in the calculation of the atomic scattering factor arises if the bound-electron scattering of the high energy x-ray photon is considered, as a result of which the atomic scattering factor becomes a complex quantity,

$$f = f_o + \Delta f' + i\Delta f'' \qquad (13)$$

where $\Delta f'$ and $\Delta f''$ are the real and imaginary correction terms for the anomalous scattering. Values of $\Delta f'$ and $\Delta f''$ for various elements corresponding to different wave-lengths are given in Int. Tables, Vol. III (1962). These correction terms are often small enough to be ignored.

If the frequency of the primary x-rays is just above that corresponding to an absorption edge of the scattering atom, the term $\Delta f''$ may be a reasonable quantity and can lead to a means of testing for the centrosymmetry of a structure and distinguishing enantiomorphic structures (Lipson and Cochran, 1966); to some extent,

it may also assist direct structure analysis (Herzenberg and Lau, 1967).

1.3.2 Temperature factor

Thermal effects cause the spreading out of the electron distribution of an atom resulting a decrease in the intensity of the scattered radiation. If f_o be the scattering factor calculated for an atom at rest, the corrected value, f, is given by

$$f = f_o \exp - B(\sin\theta/\lambda)^2 \qquad (14)$$

$$\text{or } f = f_o \exp - 8\pi^2 U(\sin\theta/\lambda)^2 \qquad (15)$$

where B is the Debye factor, which can be measured from the fundamental constants and heat capacity data (Debye, 1914), U is the mean square displacement of atom at right angles to the reflecting plane and is equal to $B/8\pi^2$, θ is the scattering angle and λ is the wave-length of the radiation. The expression (15) may lead to a fair approximation(on the assumption of spreading of the electrons in a spherical manner i.e. isotropic thermal vibration). However, due to the thermal vibration, each atom undergoes a

motion such that its electron density is spread over a small anisotropic volume, usually regarded as the triaxial ellipsoid in the general case. Each non-equivalent atom not only has a different ellipsoid, but these are also differently oriented, and hence the correction term becomes more complicated; it may be represented as (Cruickshank, 1964 and 1965 a)

$$f = f_o \exp [-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell b^*c^* + 2U_{31}\ell hc^*a^* + 2U_{12}hka^*b^*)] \quad (16)$$

where U_{ij} are with reference to the reciprocal axes a^*, b^* and c^*.

1.3.3. Lorentz, polarisation and rotation factors

The total energy, $E(hk\ell)$, of the x-ray beam reflected from a set of planes, having Miller indices h, k, ℓ of an ideally imperfect small crystal rotating with a uniform velocity can be represented as

$$E(hk\ell) = K\ L(hk\ell)\ p(hk\ell)\ |F(hk\ell)|^2 \quad (17)$$

where K = constant,

$L(hk\ell)$ = Lorentz factor,

$p(hk\ell)$ = polarisation factor,

$|F(hk\ell)|$ = structure amplitude.

The constant of the experiment, K, is given by (Buerger, 1960)

$$K = \frac{I_o \lambda^3 N^2 dV}{\omega} \cdot \frac{e^4}{m^2 c^4} \qquad (18)$$

where

I_o = intensity of the incident beam,

λ = wave-length of x-rays,

N = number of unit cells per unit volume,

dV = small volume of the crystal irradiated,

ω = angular velocity of the crystal,

e = electronic charge,

m = mass of an electron,

c = velocity of light.

Lorentz factor, $L(hk\ell)$, depends on the specific rotation of the crystal and is also dependent on the experimental method used.

The velocity of the upper layer planes is not the same as that of the equatorial layer, and allowances for rotation correction is also necessary in the calculation of the Lorentz factor for higher layer intensities. According to Tunnel (1939), the expression for the calculation of the Lorentz factor with due consideration of the rotation correction for the equi-inclination method of Weissenberg photography is

$$L(hk\ell) = 1/[2 \cos\theta (\cos^2\mu - \cos^2\theta)^{\frac{1}{2}}] \qquad (19)$$

where μ is the angle between the incident beam and the plane perpendicular to the rotation axis.

Polarisation factor, $p(hk\ell)$, is an outcome of the polarisation of the reflected x-ray beam. It is a simple function of the angle of incidence and can be written as

$$p(hk\ell) = \frac{1 + \cos 2\theta}{2} \qquad (20)$$

The energy of the diffracted beam is proportional to its intensity, $I(hk\ell)$, which can be measured by photographic methods or counter techniques and hence from eqn. (17) it can be represented

as

$$I(hk\ell) \propto L(hk\ell)\ p(hk\ell)\ |F(hk\ell)|^2 \qquad (21)$$

1.3.4 Absorption

The intensity, I, of a transmitted x-ray beam can be represented as

$$I = I_o\ \exp(-\mu t) \qquad (22)$$

where I_o is the intensity of the incident beam, μ is the linear absorption coefficient for material of the crystal depending on the wave-length of the x-radiation used, and t is the thickness of the matter through which the beam passes.

Unless the crystal is spherical or cylindrical, the absorption correction is rather complicated. If the size of the crystal is very small and the linear absorption coefficient is not high then the error due to the absorption becomes an insignificant quantity which may be ignored. Different ways and means of absorption correction applied in various methods have been dealt with by Rogers and Moffet (1956), Frasson and Bezzi (1959), Wells (1960), de Meulenaer and Tompa (1965) etc.

1.3.5 Extinction

This is the case of attenuation of the primary x-ray beam when the crystal is in a diffracting position so as to reduce the intensity of the diffracted beam. Darwin (1922) subdivided this effect into two categories, viz. "primary extinction" and "secondary extinction". Accounts of these effects have also been given by Lonsdale (1947).

1.4 STRUCTURE FACTOR AND STRUCTURE AMPLITUDE

Let there be N atoms per unit cell of a crystal, situated at points having fractional co-ordinates (x_n, y_n, z_n), referred to the crystallographic axes, a, b and c (Fig. 1.3).

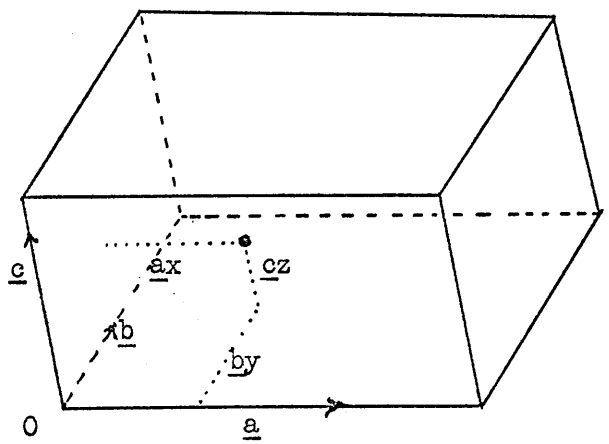


FIG. 1.3

The position of the nth atom in the unit cell can therefore be represented by the vector $\underline{R}_n$

where $\underline{R}_n = x_n\underline{a} + y_n\underline{b} + z_n\underline{c}$ (23)

From eqn. (2), the path difference between the waves scattered by these atoms will be $\lambda\underline{R}_n.\underline{S}$. Hence the contribution of the complete wave scattered by the crystal is

$$F = \sum_1^N f_n \exp \frac{2\pi i}{\lambda} \lambda\underline{R}_n.\underline{S}$$

$$\text{or } F = \sum_1^N f_n \exp 2\pi i \, \underline{R}_n.\underline{S} \quad (24)$$

Substituting $\underline{R}_n$ from (23)

$$F = \sum_1^N f_n \exp 2\pi i(x_n\underline{a}.\underline{S} + y_n\underline{b}.\underline{S} + z_n\underline{c}.\underline{S}) \quad (25)$$

Substituting the values of $\underline{a}.\underline{S}$, $\underline{b}.\underline{S}$ and $\underline{c}.\underline{S}$ from the eqn. (4)

$$F = \sum_1^N f_n \exp 2\pi i \, (hx_n + ky_n + \ell z_n) \quad (26)$$

On expansion by Euler's series ($e^{i\theta} = \cos\theta + i\sin\theta$)

$$F = \left[\sum_{1}^{N} f_n \cos 2\pi(hx_n + ky_n + \ell z_n)\right] + i\left[\sum_{1}^{N} f_n \sin 2\pi(hx_n + ky_n + \ell z_n)\right] \quad (27)$$

The quantity F is, therefore, a function of the Miller indices, (h, k, ℓ) and is called the structure factor and its modulus is known as the structure amplitude.

Substituting A and B for the terms in the two parentheses of the eqn. (27), the expression for the structure factor, $F(hk\ell)$, and the structure amplitude, $|F(hk\ell)|$, may be written as

$$F(hk\ell) = A + iB \quad (28)$$

and

$$|F(hk\ell)| = (A^2 + B^2)^{\frac{1}{2}} \quad (29)$$

The corresponding phase angle will be

$$\alpha(hk\ell) = \tan^{-1} B/A \quad (30)$$

Thus it is further evident that the structure factor is a complex quantity whereas the structure amplitude is a real number and is proportional to the intensity of the x-ray beam which itself is a measureable quantity (see eqn. 21).

To derive the expression (27), the fundamental

assumption was to consider a point atom as the source of diffraction, but it is in fact the electron cluster around the atomic nucleus which is responsible for the diffraction of x-ray beams. If $\rho(xyz)$ is assumed to be the electron density at a point (x, y, z), the amount of scattering matter in the volume element Vdxdydz is ρVdxdydz and hence the equation for the structure factor will be

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 V\rho(xyz)\ \exp 2\pi i\,(hx + ky + \ell z)\,dxdydz \qquad (31)$$

Since $\rho(xyz)$ is expressed in electronic units, the structure amplitude, $|F(hk\ell)|$, becomes a simple ratio of the contribution due to all the electrons in the unit cell to that which could be received if the contents of the unit cell were replaced by a single classical electron; hence $|F(hk\ell)|$ is a pure number.

The zero term of the series (31) becomes

$$F(000) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\,dxdydz = Z \qquad (32)$$

where Z is the total number of electrons per unit cell and for a particular compound this is a constant quantity.

1.5 FOURIER SERIES AND ITS APPLICATION IN CRYSTALLOGRAPHY

The application of Fourier series in a crystal, having its periodicity in three dimensions, was first suggested by Bragg (1915).

Allotting the integral indices h', k', ℓ' to each Fourier coefficient, K, the series can be written as

$$\rho(xyz) = \sum_{h'=-\infty}^{\infty}\sum_{k'}\sum_{\ell'} K(h'k'\ell') \exp 2\pi i(h'x + k'y + \ell'z) \qquad (33)$$

Substituting these values in eqn. (31)

$$F(hk\ell) = V \int_0^1\int_0^1\int_0^1 \sum_{h'}\sum_{k'}\sum_{\ell'=-\infty}^{\infty} K(h'k'\ell') \exp 2\pi i(h'x + k'y + \ell'z) \exp 2\pi i(hx + ky + \ell z)\, dxdydz \qquad (34)$$

The exponential functions are both periodic and the integral of their product over a single complete period is zero in general; only if $h = -h'$, $k = -k'$ and $\ell = -\ell'$, is it not zero. Under these conditions

$$F(hk\ell) = V\int_0^1\int_0^1\int_0^1 K(h'k'\ell')\, dxdydz \qquad (35)$$

i.e. $$F(hk\ell) = VK(\bar{h}\bar{k}\bar{\ell}) \qquad (36)$$

The Fourier coefficient, K, is therefore directly related to the corresponding structure factor and hence the expression for the electron density dinstribution can be written from eqn. (33)

$$\rho(xyz) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k} \sum_{\ell} F(hk\ell) \exp\left[-2\pi i(hx + ky + \ell z)\right] \qquad (37)$$

This apparently shows that the calculation of electron-density-distribution throughout the unit cell of a crystal may not be at all difficult, but due to the complex nature of the absolute value of $F(hk\ell)$ (see eqn. 31) the computation for the eqn. (37) is not an easy task.

1.6 PHASE PROBLEM AND METHODS OF SOLUTION

Equation (37) can be re-written in the form

$$\rho(xyz) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k} \sum_{\ell} |F(hk\ell)| \cos\left[2\pi(hx + ky + \ell z) - \alpha(hk\ell)\right] \qquad (38)$$

The phase angle $\alpha(hk\ell)$ is the same as shown in eqn. (30). No experimental method can record the value of $\alpha(hk\ell)$. The great difficulty in determining its value has caused crystallographers to call this trouble "the phase problem". The following are some of the important techniques of determining the unknown phases.

1.6.1 Trial and error method

The basic idea of this method is to postulate a certain atomic arrangement that conforms to the space group symmetry and to calculate the corresponding structure amplitudes, $|F_c|$, and to compare these with the observed values, $|F_o|$, so as to decide whether the structure will be acceptable or not.

It has been found useful to express the overall agreement in terms of the mean discrepancy, the so called "residual",

$$R = \frac{\sum \left| |F_o| - |F_c| \right|}{\sum |F_o|} \qquad (39)$$

where the summation is to be taken over all the reflections (Booth, 1945). If the agreement be reasonable (say $R < 0.45$), the structure may be considered as a promising one and the adjustment may be continued until the correct result is obtained.

The trial structures are arrived at by various methods viz. consideration of symmetry and atomic radii, evidence from various physical properties (morphology and cleavage, infra-red absorption, optical and magnetic properties etc.), distribution of x-ray intensities, experience gained from other similar crystals and so on.

To minimise the calculations, use of the Fourier transform of a set of atoms, is found helpful. In this method holes representing the atomic locations in projection of the proposed structure and the atomic types are punched on a mask. The diffraction in parallel light represents the required Fourier transform and this can be compared with the corresponding weighted reciprocal lattice. In this way probable structures can be quickly tested and hence the number of possibilities may be reduced to a manageable quantity.

1.6.2 Patterson function

Patterson (1935) showed that important information can be derived from the phaseless quantities, $|F|^2$. He set out to solve the function, P(uvw), called the Patterson function, where

$$P(uvw) = V \int_0^1 \int_0^1 \int_0^1 \rho(xyz)\ \rho(x+u,\ y+v,\ z+w)\ dxdydz \qquad (40)$$

Substituting in this expression the value of $\rho(xyz)$ from eqn. (37) and considering the same reasoning as was applied to obtain eqn. (35) from that of (34) it can be shown that

$$P(uvw) = \frac{1}{V} \sum_{-\infty}^{\infty} \sum \sum \left| F(hk\ell) \right|^2 \exp 2\pi i(hu+kv+\ell w) \qquad (41)$$

$$\text{or } P(uvw) = \frac{1}{V} \sum_{h} \sum_{k}^{\infty} \sum_{\ell} \left|F(hk\ell)\right|^2 \cos 2\pi (hu + kv + \ell w) \qquad (42)$$

In this equation $\left|F(hk\ell)\right|^2$ is the product of $F(hk\ell)$ and its complex conjugate $F(\bar{h}\bar{k}\bar{\ell})$ and the function P(uvw) is real for all values of u, v, w. Eqn. (37) represents the peaks in the atomic locations whereas eqn. (42) has its peaks at the endsof the vectors between atomic locations. The height of every peak is proportional to the product of the atomic numbersof atoms involved in the vector. The structure amplitudes are derived directly from the measureable quantity, the intensity data. Therefore, the Patterson synthesis can be computed without much trouble and hence simple structures having a limited number of atoms, may be solved directly from the Patterson function. Since there are N(N-1) distinct interatomic vectors (corresponding to the N atoms per unit cell), which are also revealed in the Patterson synthesis, it is very difficult to obtain the positions of all the atoms of even a moderatly complicated structure by inspection of the Patterson function alone.

It was Harker (1936), who for the first time correlated the Patterson function with the electron density distribution.

He pointed out that certain symmetry related planes or lines (called Harker sections or Harker lines) in the three dimensional Patterson synthesis contain more useful information about the structure. Buerger (1951), in his minimum function method showed that if two Patterson maps are superimposed and a third map is drawn over the minimum contours of the coincident peaks, it may reveal the identity of the molecule.

1.6.3 Heavy atom method

If the crystal asymmetric unit contains a few heavy atoms whose scattering power dominates the intensity, it may control some or all the phases. The positions of heavy atoms, if not too many, can easily be obtained from the Patterson function and hence the phases due to the heavy atoms can be calculated. Taking these as the actual phases due to the whole contents of the cell, an electron density distribution can be computed which may reveal some of the light atoms. Inclusion of these new atoms in a subsequent structure factor calculation will yield improved phase angles which can be used with the observed structure amplitudes to give a still better

electron density distribution. Through several cycles of such calculations, it may be possible to elucidate a complicated structure. The first successful application of the heavy atom method was by Robertson and Woodward (1940) in solving the structure of platinum phthalocyanine.

Though this is a very powerful method, it also has its limitations. If the heavy atom is too heavy, light atoms may not be revealed in the electron density distributions based on only the heavy atom phases. In such circumstances, if the light atoms are revealed at all, their positions will be rather uncertain. On the other hand, if the heavy atom is not heavy enough then the phase contributions from it may not be able to show the positions of the light atoms at all. A reasonable compromise is achieved when the sum of the squares of the atomic numbers of the heavy atoms is equal to that of the lighter atoms (Lipson and Cochran, 1966). Sim (1961) has shown the proportion of correct signs in the heavy atom method in terms of γ defined as

$$\gamma = \frac{\sum f_H^2}{\sum f_L^2} \qquad (43)$$

where f_H and f_L are the scattering factors of the heavy and light atoms respectively.

In the heavy atom method, further complications arise when the heavy atom is situated in a special position such that it makes little or no contribution to a proportion of the structure factors. The ensuing electron density distribution based on heavy atom phases is then complicated by pseudo-symmetry and its interpretations may be difficult.

1.6.4 Isomorphous replacement method

Another powerful method of solving the phase problem, first used by Cork (1927), is to compare the x-ray intensities from a series of isomorphous compounds in which one atom is replaced by another. The first successful application of this technique in a large organic compound, phthalocyanine, was by Robertson (1935, 1936). The popularity of this method grew rapidly being very useful in the structure elucidation of penicillin (Crowfoot et al. 1949). In this method, unlike the heavy atom technique, the size of the

replaceable atom is immaterial. The only consideration is to have all sets of intensity data on the same scale (Beevers and Cochran, 1947).

Let the compositions of two isomorphous compounds be PR and QR where P and Q are the replaceable atoms and R is the remainder of the molecule.

$$\text{Then } \underline{F(PR)} - \underline{F(QR)} = \underline{F(P)} - \underline{F(Q)} = \underline{\Delta F} \qquad (44)$$

For centro-symmetric crystals structure factors, $\underline{F}$, are real quantities which are either positive or negative and $\underline{\Delta F}$ is equal to the difference in the scattering powers of the two replaceable atoms; and hence it is not difficult to determine the signs of $\underline{F(PR)}$ and $\underline{F(QR)}$, especially, if the replaceable atoms are situated at a symmetry centre.

In the non-centro-symmetric case the $\underline{F}$s are complex quantities whose magnitudes are known but not the phases. Corresponding to a particular value of $\underline{\Delta F}$ one pair of solutions for $\underline{F(PR)}$, $\underline{F(QR)}$ having the same magnitude but opposite phase are obtained (Fig. 1.4).

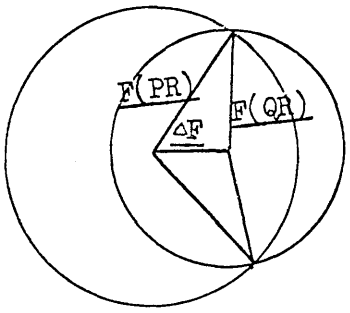


FIG. 1.4

To decide the final result, further information is necessary which can be made available through double isomorphous replacement as suggested by Bokhoven et al. (1951) and is further elaborated by Harker (1956). The multiple isomorphous replacement method has been used with great success in determining the structures of proteins (Avey et al. 1967).

1.6.5 Direct methods

A number of direct methods of phase determination have been suggested by different authors. Of these, Harker and Kasper's (1947, 1948) method of inequalities deals with the relation between

structure factors, while Sayre's (1952) sign relation method is based on the novel idea of a squared atom. Karle and Hauptman (1950, also Hauptman and Karle, 1950) have introduced a powerful statistical method which was successful in solving the structure of p, p'-dimethoxybenzophenone (Karle et al. 1958). The symbolic addition procedure for obtaining phases directly from the structure factor magnitudes has also been applied by Karle and Karle (1966) to the structure determination of Alkaloid Panamine.

1.7 STRUCTURE REFINEMENT

The methods of solving a structure, so far discussed, can only lead to the approximate atomic parameters. The next task is to refine the parameters so that the discrepancy between the observed and calculated structure amplitudes becomes a minimum.

1.7.1 Fourier methods

1.7.1.1 Successive electron density distribution

The method of successive structure factor calculation and computation of electron density distribution can be applied for

refining a crude structure. In this technique, solution and refinement both may go hand in hand, especially, in the heavy-atom method, where gradual inclusion of recognisable atomic parameters improves the resultant electron density distributions. After the full structure is solved, the process is repeated until the changes in atomic parameters are insignificant.

The major drawback of this method is the series termination error which is due to the inclusion of only a limited number of Fourier terms in the calculation of the electron density distribution. To minimise this error, co-ordinates for each atom are obtained from the two electron density distributions — one with F_o as Fourier coefficients and the other with F_c. The corrected co-ordinates can be calculated from the expression (Booth 1946 b)

$$X_{corr} = X_{old} + X_{F_o} - X_{F_c} \qquad (45)$$

where X_{corr} = corrected co-ordinate,

X_{old} = old co-ordinate,

X_{F_o} = co-ordinate from F_o map,

X_{F_c} = co-ordinate from F_c map.

The correction for series termination error is appreciable and may amount to 0.01 to 0.04 Å (Burger, 1960).

1.7.1.2 Difference synthesis

The full difference synthesis $(F_o - F_c)$ was first suggested as a device for refinement by Booth (1948b). If the proposed structure is quite close to the actual one, in the difference map flat topography is expected, except some undulatory characteristics due to random error. In this process refinement of both the positional and thermal parameters is possible. This method is free from the error due to the series termination effect and can be used for checking the types of thermal vibration and drastic error in the atomic positions, and may also be used to obtain the approximate positions of the lighter atoms which are not revealed in the ordinary electron density distribution.

In order to achieve better results from the Fourier method and to generalise the difference synthesis Cruickshank (1952) has introduced a modified technique which is almost identical to the least squares methods. In this process an attempt is made to minimise

the quantity, D, where

$$D = \frac{1}{V} \sum_{hk\ell} (|F_o| - |F_c|) \cos [2\pi(hx + ky + \ell z) - \alpha(hk\ell)] \qquad (46)$$

1.7.2 Least squares methods

The refinement of atomic parameters with the help of the least squares methodswas first suggested by Hughes (1941). The basic idea of this method is to establish sets of normal equations and find the parameters p_j which minimise the quantity

$$R = \sum w \Delta^2 \qquad (47)$$

where w = weight allotted to the observation.

and $\Delta = |F_o| - |F_c|$, and the sum is taken over all the independent structure amplitudes.

For R to be the minimum

$\frac{\partial R}{\partial p_j} = 0$ where j = 0, 1, 2..... n parameters in the determination of F_c.

$$\text{i.e. } \sum w \Delta \frac{\partial |F_c|}{\partial p_j} = 0 \qquad (48)$$

If p_j be close to the correct value and ℓ_i is a small change in the parameter p_i then it can be shown that

$$\sum_{i=1}^{n} \left[\sum_{hk\ell} w \frac{\partial |F_c|}{\partial p_i} \frac{\partial |F_c|}{\partial p_j} \right] \ell_i = \sum_{hk\ell} w \Delta \frac{\partial |F_c|}{\partial p_j} \qquad (49)$$

for each value of $j = 0, 1, \ldots\ldots n$, n equations may be set up to determine the n unknown quantities. They may be written out as

$$\left.\begin{aligned} &\sum w \left(\frac{\partial |F|}{\partial p_1}\right)^2 \ell_1 + \sum w \left(\frac{\partial |F|}{\partial p_1}\right)\left(\frac{\partial |F|}{\partial p_2}\right) \ell_2 + \ldots\ldots = \sum w \Delta \frac{\partial |F|}{\partial p_1} \\ &\sum w \left(\frac{\partial |F|}{\partial p_1}\right)\left(\frac{\partial |F|}{\partial p_2}\right) \ell_1 + \sum w \left(\frac{\partial |F|}{\partial p_2}\right)^2 \ell_2 + \ldots\ldots = \sum w \Delta \frac{\partial |F|}{\partial p_2} \\ &\ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \end{aligned}\right\} \qquad (50)$$

These are called the normal equations of least squares. For structure refinement, these simultaneous equations are solved to adjust the parameters so that the corrections become small in comparison with the estimated standard deviations. Thus positional, thermal and scale parameters may be improved.

The main advantage of the least squares methodsof structure refinement is that in this process weight may be assigned

to the reflections according to their reliability and the method is free from series termination errors.

1.7.3 Minimum residual method

Refinement of a crystal structure by direct calculation of the minimum residual was first introduced by Bhuiya and Stanley (1963). In this method, the parameter to be refined is varied in turn from $p_j + n\Delta p_j$ to $p_j - n\Delta p_j$ in $2n + 1$ steps of Δp_j and the accepted refined value is that which gives the minimum value of the residual, R, where $R = \frac{\sum\left||F_o| - |F_c|\right|}{\sum|F_o|}$. This method was used in the refinement of the structure of 2-chloro-1, 8-phthaloylnaphthalene in the (100) projection (section II, chapter 4).

1.7.4 Other methods

There are some other methods of refining the atomic parameters. In the process of differential synthesis (Booth, 1946 a) it is assumed that at the point of maximum electron density

$$\frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial y} = \frac{\partial \rho}{\partial z} = 0 \qquad (51)$$

with this basic concept, differential equations are set up for obtaining the improved atomic parameters. In the method of steepest descents (Booth, 1947 b and 1949) an attempt is made to minimise the figure of merit, R, where

$$\begin{aligned} R &= \left(|F_o| - |F_c| \right) \\ R' &= (F_o - F_c)^2 \\ R'' &= \left(|F_o| - |F_c| \right)^2 \\ R''' &= \left(|F_o|^2 - |F_c|^2 \right)^2 \end{aligned} \qquad (52)$$

1.8 EVALUATION OF ACCURACY

1.8.1 Residual

The extent of accuracy of a structure is usually judged by the value of the residual,

$$R = \frac{\Sigma\left|\,|F_o| - |F_c|\,\right|}{\Sigma|F_o|} \tag{53}$$

In the refinement by the least squares methods

$$R = \frac{1}{a^2} \Sigma w\Delta^2 \tag{54}$$

where a = scale factor of $|F_o|$

w = weight allotted to the observation

$\Delta = a|F_o| - |F_c|$

It is normally expected that the smaller the value of R, the better is the structure determination. Hamilton (1965) has given a thorough analysis of the R factor and the accuracy of the structure. Cruickshank (1964) has introduced another index of comparing the degree of refinement

$$R' = \frac{\Sigma w \Delta^2}{\Sigma w (a |F_o|)^2} \qquad (55)$$

1.8.2 Standard deviations of parameters

Another criterion of judging the accuracy of the structure determination, is to calculate the standard deviations of the parameters which can be derived from least squares residual by application of the equation

$$\sigma(p_j) = \frac{\Sigma w \Delta^2}{(m - n) \Sigma \left(\frac{\partial |F_c|}{\partial p_j} \right)} \qquad (56)$$

where m and n are the numbers of independent observations and parameters to be refined.

1.8.3 Standard deviations of bond lengths

The standard deviation of the bond length PQ may be defined as

$$\sigma^2(\ell) = \sigma^2(P) + \sigma^2(Q) \qquad (57)$$

where $\sigma^2(P)$ and $\sigma^2(Q)$ are the variance of P and Q in the direction of PQ. If the atoms are related by a mirror plane or a centre of symmetry

$$\sigma(\ell) = 2\sigma(P) \qquad (58)$$

1.8.4 Standard deviations of bond angles

If β be the angle subtended at Q by the three independent atoms P, Q and R, then the variance

$$\sigma^2(\beta) = \frac{\sigma^2(P)}{PQ^2} + \sigma^2(Q)\left(\frac{1}{PQ^2} - \frac{2\cos\beta}{PQ.QR} + \frac{1}{QR^2}\right) + \frac{\sigma^2(R)}{QR^2} \qquad (59)$$

In the above expression $\sigma^2(P)$ and $\sigma^2(R)$ are the variance of P and R in the plane PQR and perpendicular to PQ and QR, and $\sigma^2(Q)$ is the variance of Q in the direction tangential to the circle PQR (Darlow, 1960).

1.8.5 Calculated mean planes and χ^2 test

Another method of judging the accuracy of a structure is to calculate a series of mean planes through the atoms (Schomaker et al.,1959) which are expected to be coplanar and to decide the merit of the results. In this respect the χ^2 test may be used to decide the goodness of the fit of the experimental result to their theoretical values.

Let D_j be the deviation (in $\overset{o}{A}$) of jth atom from the calculated mean plane through n atoms and σ is the mean deviation (in $\overset{o}{A}$) in the positional parameters of the atoms, then

$$\chi^2 = \sum_1^n \left(\frac{D_j}{\sigma}\right)^2 \qquad (60)$$

The probability of the deviation from the planarity due to the random experimental error can then be examined from the χ^2 tables (Fisher and Yates, 1953). If the probability that the plane is a good fit be less than 1% it is usually safe to assume that the atoms are non-planar.

1.9 COMPUTATION

The many calculations were performed on the Glasgow University KDF-9 computer. Some details of programs and authors are given below:-

PROGRAM	AUTHOR
Intensity correction (I to $\|F_o\|$)	A. A. Hook R. Truter and M. Wells
Isotropic structure factor and Fourier	J. G. Sime
Fourier search	D. McGregor
Least squares refinement	D.W.J. Cruickshank and J. G. F. Smith
Bond length and bond angle	K. W. Muir
Data sharpening for Patterson function	K. W. Muir
Minimum residual refinement	K. W. Muir
Hydrogen placing	G. Ferguson
Mean plane	W. Oberhänsli

PROGRAM - contd.	AUTHOR - contd.
Standard deviations of bond lengths and bond angles	W. S. Macdonald
Sim weight	K. W. Muir and D. R. Pollard

It was necessary to modify some of the programs to suit specific examples and to write small programs for various calculations and data handling.

SECTION II

CRYSTAL STRUCTURES OF SOME *o*-HALOGENO-AROYL COMPOUNDS

2. INTRODUCTION

The steric effects occasioned by the close proximity of a halogen atom and a neighbouring group are susceptible to investigations by a variety of physical methods e.g. i.r., u.v., n.m.r., diffraction methods etc. Only diffraction methods allow precise determination of intramolecular distances in anything other than the small molecules and in addition, in monohalogeno compound the halogen atom normally provides a means of overcoming the crystallographic "phase problem".

Ferguson and Sim have investigated a number of o-monohalogeno benzoic acids [o-chlorobenzoic acid(Ferguson and Sim, 1961), o-bromobenzoic acid (Ferguson and Sim, 1962 a) and 2-chloro-5-nitrobenzoic acid (Ferguson and Sim, 1962 b)]. All these structures showed significant non-planarity and distortions of bond angles, which might be the outcome of the intramolecular overcrowding. Another interesting feature in the structures, was the presence of intermolecular hydrogen bonds.

The first x-ray study of the hydrogen bond was done by Bernal and Fowler (1933). Since then crystallographers have done much work in this field. Fuller (1959), Baur (1965), Speakman (1967) and others have reviewed some of these works.

Normally, the hydrogen bond (A-H...B) is assumed to be linear and in a large number of compounds (Hamilton, 1962), the $\widehat{A\text{-}H}...B$ angle is found to be near to 180°. The existence of deviations from linearity indicates that the energy required to bend the hydrogen bond is not large and can be compared to the energy of the van der Waals interactions in the crystal. The hydrogen bond is thus more readily distorted by packing forces than any covalent bond. The major characteristics of the hydrogen bond are decided by the type and chemical environment of the donor and acceptor atoms. Because of its small bond energy (only about 5 K.cal./mole) and the small activation energy involved in its formation and rupture, the hydrogen bond is especially suited to play an important role in reactions occurring at normal temperature. For this reason it has been extensively studied by different methods (Pimental and McClellan, 1960).

Various hydrogen bonds of the type OH...O, NH...O, OH...N, NH...N etc. have been investigated thoroughly (Fuller, 1959; Baur, 1965), but there has been very little systematic study of CH...O or CH...N hydrogen bonds in the solid state. The apparent unusually short intermolecular CH...O contact of 3.0 Å, in the crystal structure of 1, 3, 7, 9-tetramethyluric acid (Sutor, 1963 a) prompted Sutor (1963 b) to review crystallographic works on structures having short CH...O contacts. In her review, she could not find any structures having intermolecular ethynyl hydrogen bonds. Tyrrell (1963) carried out investigations of ethynyl hydrogen bonds in benzoylacetylenes and phenylacetylenes by various methods.

The main purpose of the following investigations of the four mono-halogene-aroyl compounds (o-chlorobenzoylacetylene, o-bromobenzoylacetylene, o-fluorobenzoic acid and 2-chloro-1, 8-phthaloylnaphthalene) was to extend the number of the members of the series investigated, and to examine the common features of conformation, intermolecular hydrogen bonds and intramolecular overcrowding in the family of o-halogeno-aroyl compounds. The detailed findings are discussed in Chapter 5.

CHAPTER 1

o-CHLOROBENZOYLACETYLENE

2.1 INTRODUCTION

During his investigations of ethynyl hydrogen bonds by various means, Tyrrell (1963) prepared o-chloro- and o-bromo-benzoylacetylenes. These were prepared in two stages; the first being the synthesis of halogeno-benzoylcarbinol and the second, the oxidation of the carbinol.

In the infra-red absorption spectrum of o-chlorobenzoyl-acetylene, a maximum corresponding to the ethynyl hydrogen stretching frequency occurs at 3304 $cm.^{-1}$ in cyclohexane solution and at 3235 $cm.^{-1}$ in the solid state. It was inferred from this (Tyrrell, 1963) that there is some additional bonding involving this group in the solid state which is not present in solution. The characteristic studies show that the hydrogen bonding in the benzoyl-acetylene is surprisingly strong (Brand, Eglinton and Tyrrell, 1965). This is confirmed by the following crystal structure analysis (Ferguson and Islam, 1966 a).

2.1.1 Crystal data

o-Chlorobenzoylacetylene, C_9H_5OCl, M = 164.5, a = 3.97 ± 0.02, b = 12.35 ± 0.04, c = 15.87 ± 0.04 Å, β = 98.4 ± 0.2°, U = 769.8 Å^3, Dm = 1.40 gm/cc. (by flotation), Z = 4, Dc = 1.42 gm/cc., F(000) = 336, space group $P2_1/c$ (C_{2h}^5, No.14, Int. Tables, Vol. I, 1965); linear absorption coefficient for x-rays (λ = 1.542 Å), μ = 43 cm.$^{-1}$.

o-Chlorobenzoyl acetylene crystalises from methanol and water mixture as needles elongated along the a-axis. The unit cell dimensions were measured from the oscillation and equatorial layer Weissenberg photographs, and hk0 and h0ℓ precession photographs.

2.1.2 Space group

0kℓ — 3kℓ Weissenberg photographs and precession photographs of the hk0 and h0ℓ reciprocal lattice nets were examined and it was found that the h0ℓ spectra were absent when ℓ = 2n + 1 and that the 0k0 spectra were absent when k = 2n + 1, but there was no restriction for the general reflections. The monoclinic character of the crystal was already established. The

space group is therefore, $P2_1/c$ (C_{2h}^5, Int. Tables, Vol. I, 1965) having the general equivalent positions

$$x,\ y,\ z. \tag{1}$$

$$-x,\ -y,\ -z. \tag{2}$$

$$-x,\ \tfrac{1}{2}+y,\ \tfrac{1}{2}-z. \tag{3}$$

$$x,\ \tfrac{1}{2}-y,\ \tfrac{1}{2}+z. \tag{4}$$

2.1.3 Intensity data

Since the crystals sublimed readily on exposure to the atmosphere, a small needle crystal enclosed in a Lindemann glass capillary was used for collecting intensity data. The intensities of reflections of the reciprocal lattice nets $0k\ell$ to $3k\ell$ were recorded on equatorial and equi-inclination Weissenberg photographs using Cu Kα radiation ($\lambda = 1.542$ Å). The multiple film technique of Robertson (1943) was employed. For the $0k\ell$ and $1k\ell$ reciprocal lattice nets two sets of photographs (each of a four film-pack) were taken, one of a long exposure and the another of a short exposure, so as to facilitate the visual estimation of a wide range of intensities. The $2k\ell$ and $3k\ell$ nets were photographed

on one pack of four films. The visual estimation of 772 independent reflections was carried out using a calibrated intensity step wedge; a further 332 "unobserved" reflections were included in all calculations with a value one half of the minimum locally observable. Initially, all the intensities were placed on approximately the same scale by comparing the times of exposure. The intensities were corrected for appropriate Lorentz, polarisation and rotation factors (See Sec. I, 1.3.3). The absorption corrections were ignored.

The ratio of the square of the atomic number of the heavy atom to the sum of the squares of the atomic numbers of the rest of the atoms per asymmetric unit is

$$\gamma = \frac{f_H^2}{\Sigma f_R^2} = 0.74 \qquad (5)$$

which showed that the heavy atom method for phase determination might be favourable (Lipson and Cochran, 1966).

2.1.4 Structure determination and refinement in the (100) projection

Because of the short a axis (3.97 Å) it was expected that there would be good resolution of the atoms in the (100) projection; while the full three dimensional data collection was in progress, the structure was solved and refined in the (100) projection using the 230 0kℓ data.

The plane group of $P2_1/c$ in the (100) projection is pgg (Int. Tables, Vol. I, 1965) having the equivalent positions

$$y, \quad z \tag{6}$$

$$-y, \quad -z \tag{7}$$

$$\tfrac{1}{2} + y, \quad \tfrac{1}{2} - z \tag{8}$$

$$\tfrac{1}{2} - y, \quad \tfrac{1}{2} + z \tag{9}$$

This shows that in the (100) projection of the Patterson synthesis peaks corresponding to the vectors between the heavy atoms will be at (2y, 2z), $(\tfrac{1}{2} - 2y, \tfrac{1}{2})$ and $(\tfrac{1}{2}, \tfrac{1}{2} - 2z)$. In the (100) Patterson projection (Fig. 1.1) peaks "A", "B" and "C" correspond to the above interpretation and were confirmed to be Cl - Cl vector peaks.

Two maps of the Patterson projection were prepared on tracing paper using two contrasting colours. The general Cl - Cl vector peak "A" of one was then superimposed on the origin of the other. The minimum function map (Fig. 1.2) was then prepared (Buerger, 1951). It clearly revealed the positions of all the non-hydrogen atoms.

An approximate scale factor and overall thermal parameters for the atoms were then found from a Wilson plot (Wilson, 1942). Two cycles of refinement by successive electron density calculations were then followed by the correction for the series termination error (See Sec. I, 1.7.1.1). The least squares refinement for adjustment of positional and isotropic thermal parameters converged at R = 0.09. Using the refined scale factor the 0kℓ data were then placed on the absolute scale.

2.1.5 Structure determination in three dimentions

From equivalent positions (1) and (3) of the space group $P2_1/c$ it is evident that the end locations of some of the interatomic vectors will be at $(2x, \frac{1}{2}, \frac{1}{2} + 2z)$. This indicates that the Harker section (See Sec. I, 1.6.2) at $v = \frac{1}{2}$ should contain a Cl - Cl vector

peak. In the Harker section (Fig. 1.3) one peak was seen to be dominating. The z co-ordinate of this peak agreed quite well with that of the Cl atom found in the projection work. This decided the unknown x co-ordinate for the chlorine atom; accurate y and z co-ordinates for the rest of the non-hydrogen atoms were already known. The x co-ordinates for the carbon atoms of the benzene ring and C(7) of the carbonyl group were derived from the geometrical considerations, paying due regard to the tilt of the benzene ring as given by the (100) projection.

Structure factors were computed with all 1104 reflections using calculated x and refined y and z co-ordinates for C(1) — C(7) and Cl atoms. The overall R factor became 0.388 and for 0kℓ planes alone the residual was 0.424. The exclusion of two acetylenic carbons [C(8) and C(9)] and one carbonyl oxygen was the cause of such a high R factor. The first electron density distribution was then computed with all the data; the 230 0kℓ planes were correctly phased from the projection work and the rest were phased from the eight atoms structure factor calculation as mentioned earlier. In the map the improved locations of the eight atoms were

seen to be accompanied by the clear peaks of the remaining atoms [C(8), C(9) and O]. The peak positions for all the eleven non-hydrogen atoms were then calculated from this electron density distribution by Booth's method (Booth, 1948 a). At this stage the residual, R, was 0.18. The course of the structure solution is shown in Table 1.1.

2.1.6 Structure refinement

Two cycles of Fourier refinement were carried out at the end of which no appreciable change in the atomic parameters were noticed. In a Fourier synthesis using $(F_o - F_c)$ as coefficients, peaks attributed to hydrogen atoms and anisotropic characteristics of the other atoms were noticed; the absence of any other significant peaks confirmed the correctness of the structure. The R factor was 0.176. The appropriate correction for the error due to the series termination effect, which is inherent in the normal refinement by Fourier method, was then applied (See Sec. I, 1.7.1.1).

In the structure factor calculations the Uiso values from the projection refinement were used. At the conclusion of Fourier refinement the intensity data for the individual layers were then scaled so that $K \sum |F_o| = \sum |F_c|$. No later alteration of these layer scale factors was found necessary; only an overall scale factor was subsequently refined.

Altogether twelve cycles of least squares refinement were required to adjust the atomic parameters and scale factor. The progress of least squares refinement is shown in Table 1.2. At the end of the twelfth cycle, parameter shifts were all less than one third of their estimated standard deviations, indicating the convergence of the refinement. The final R factor was 0.092. The calculated structure factors, at the end of refinement, are shown in Table 1.3.

In the first three cycles of full matrix least squares refinement, adjustments were made to the positional and isotropic thermal parameters for all non-hydrogen atoms and the overall scale factor. The individual layer scales (K) and residuals (R) for each of the four layers, $0k\ell$ - $3k\ell$, were calculated by making $K\Sigma|F_o| = \Sigma|F_c|$

but no significant difference in individual layer scales was noticed. The positions of the four benzene ring hydrogens and one acetylenic hydrogen were calculated from geometrical considerations using the standard bond length of an aromatic C-H, 1.084 and an acetylenic C-H, 1.06 Å respectively. These hydrogen co-ordinates were then introduced in the subsequent structure factor calculations but were not refined. The same isotropic temperature factor, Uiso = 0.044, was used for all the hydrogen atoms. In the remaining cycles of refinement, anisotropic thermal vibrations for the eleven non-hydrogen atoms were allowed and a block diagonal approximation for the normal equations was used. In all stages of refinement, the weighting scheme applied, was that of Cruickshank et al. (1961).

$$\sqrt{w} = 1/(p_1 + |F| + p_2|F|^2)^{\frac{1}{2}} \qquad (10)$$

Up to the seventh cycle of refinement, the values of the constants, p_1 and p_2, were chosen to be $2|F|_{min.}$ and $2/|F|_{max.}$ respectively. A correct choice of weighting scheme should give approximately the same mean value of $\sum w\Delta^2$ for all batches of data grouped in the

order of increasing $|F_o|$ and $\sin\theta/\lambda$. From such an examination a change of the value of the constant, p_1 from 4 to 6 was found necessary. After one further cycle of refinement, while R was 0.11, the agreement of the whole sets of $|F_o|$ and $|F_c|$ were thoroughly checked and twelve low order high intensities were found to have very bad agreement. After independently remeasuring the intensities of these planes and allowing for approximate spot shape corrections, the planes were again introduced into the refinement cycles. Further adjustment of the weighting scheme was found necessary and consequently, the value of p_1 was changed to 8. The hydrogen positions were then picked out from a three dimensional $(F_o - F_c')$ Fourier synthesis, (where F_c' represents the calculated structure factors for non-hydrogen atoms only) and were included in the last three cycles of refinement but no attempt was made to refine their parameters.

At the end of the twelfth cycle of the least squares refinement, the parameter shifts were quite negligible in comparison with the appropriate estimated standard deviations indicating the

convergence of the refinement. Once again structure factors were calculated for non-hydrogen atoms and a difference synthesis was computed. In the map well resolved hydrogen peaks were observed in the expected locations but no other significant features were noticed. The relevant sections for the hydrogen positions of the difference synthesis are shown in Fig. 1.4, superimposed on the sections of the third three dimensional electron density distribution.

In all the structure factor calculations, atomic scattering curves used were those of Int. Tables, Vol. III (1962).

2.1.7 Final atomic parameters, molecular dimensions etc.

The Patterson projection, the minimum function map and the Harker section are shown in Figures 1.1, 1.2 and 1.3 respectively. The final three dimensional electron density distribution of the atoms and the hydrogen locations from the last difference synthesis are presented in Fig. 1.4, as superimposed contour sections drawn parallel to (100). The arrangement of the molecules viewed along the short a-axis is shown in Fig. 1.5. Bond lengths and angles are in Fig. 1.6. This also contains the

numbering scheme for identifying the atoms of a molecule. The distances and angles involved in the intermolecular hydrogen bonding is presented in Fig. 1.7.

The course of the structure solution, progress of refinement and the structure factor agreements are shown in Tables 1.1, 1.2 and 1.3 respectively. The final fractional co-ordinates and estimated standard deviations of the non-hydrogen atoms, are in Table 1.4. In the Table 1.5, there are the fractional co-ordinates of hydrogen atoms calculated from the last difference synthesis. The orthogonal co-ordinates of the atoms, referred to the axes parallel to a^*, b and c, and the corresponding estimated standard deviations (in $\mathring{A}$) are shown in Table 1.6. The anisotropic temperature factors are in Table 1.7. These are the values of U_{ij} (See Sec. I, 1.3.2.). The principal values and the direction cosines of the vibration tensors with reference to the orthogonal axes parallel to a^*, b and c are presented in Table 1.8. Some intramolecular and intermolecular short distances can be seen in Table 1.9. Deviations of atoms from various mean planes are given in Table 1.10.

The average estimated standard deviations, derived from the least squares normal equations, of bond lengths are, Carbon-Carbon (0.009), Carbon-Oxygen (0.007) and Carbon-Chlorine (0.006 Å). The average estimated standard deviation of bond angles is 0.6°.

DIAGRAMS AND TABLES

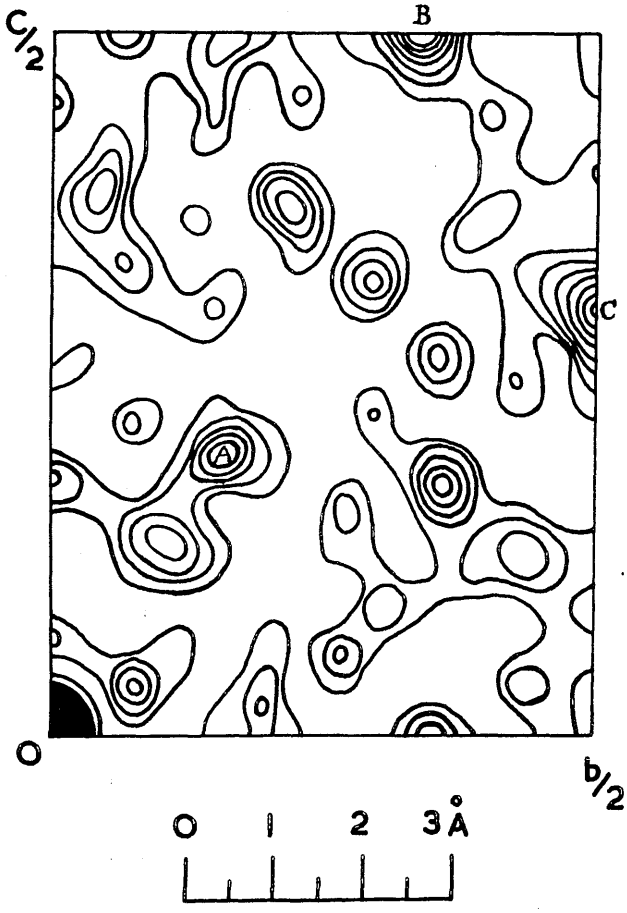


FIG. 1.1

The Patterson projection on to (100). Contours are at arbitrary intervals.

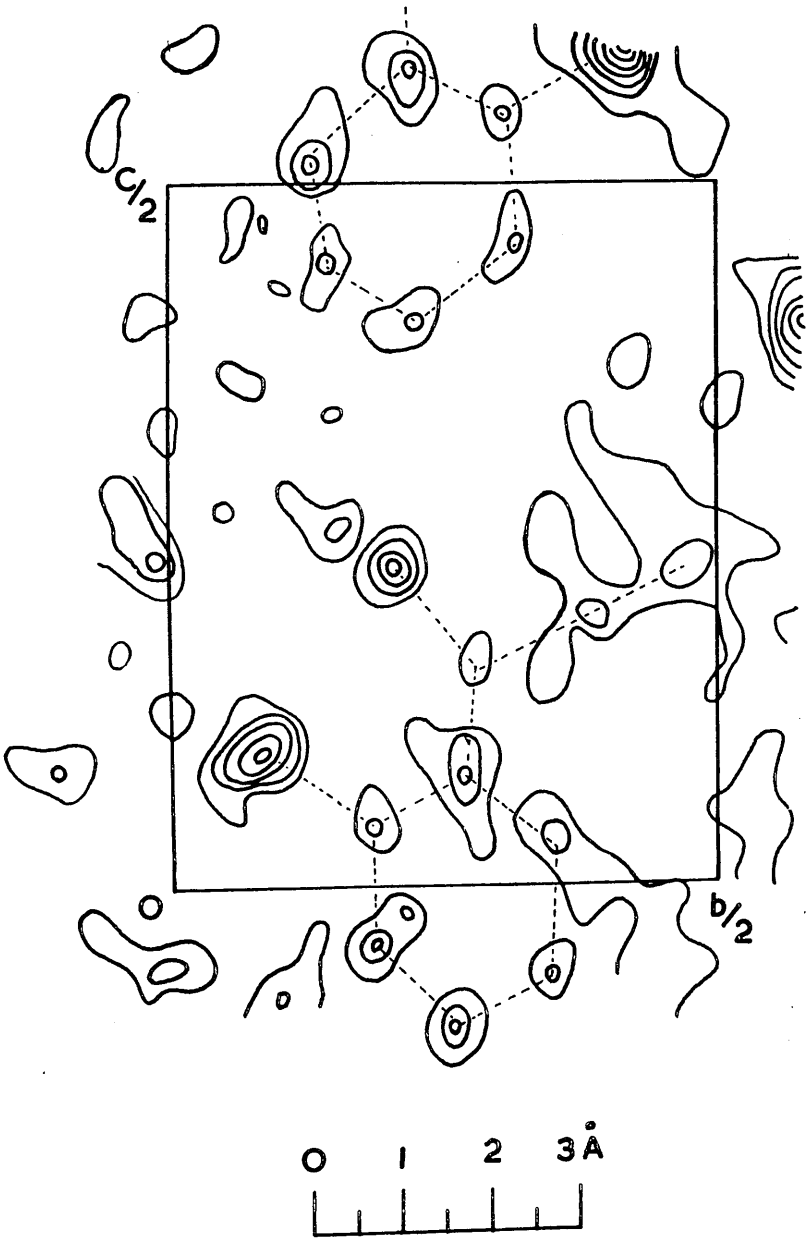


FIG. 1.2

The minimum function in projection on (100) obtained from superimposition of the Cl-Cl vectors in (100) Patterson synthesis and its interpretation.

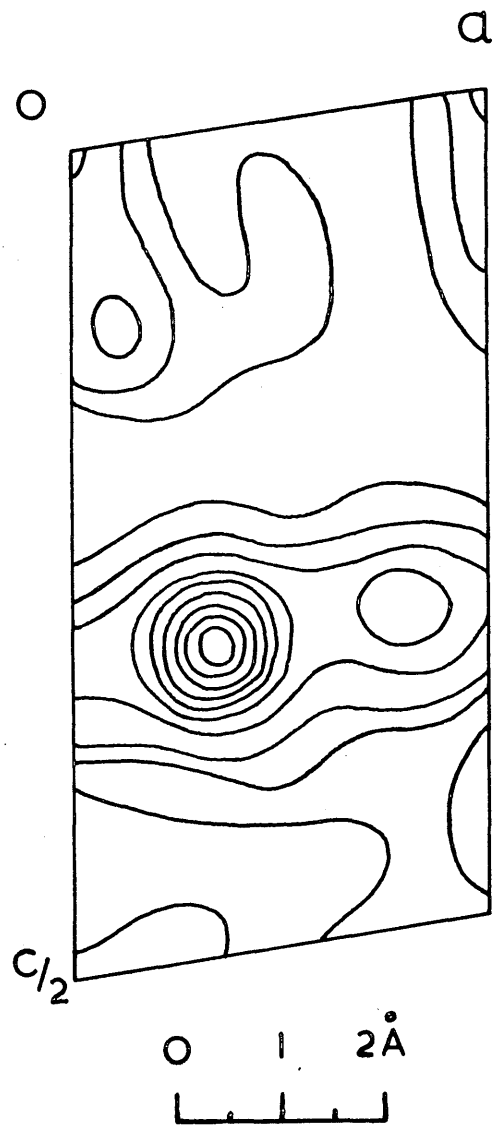


FIG. 1.3

The Harker section at v = 0.5. Contours are at arbitrary intervals.

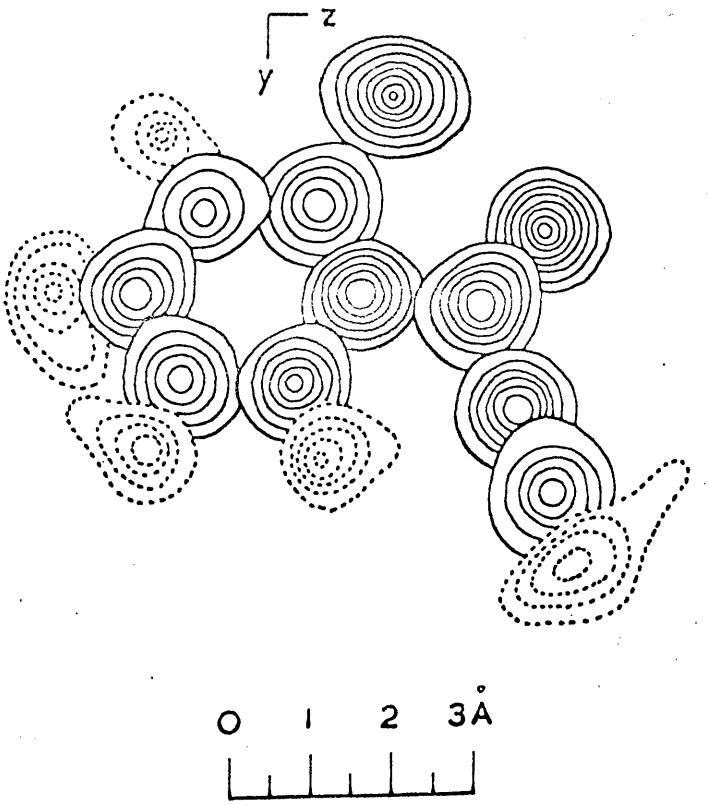


FIG. 1.4

The third electron density distribution (solid contours) shown by means of superimposed contour sections parallel to (100). Also shown are the hydrogen peaks (broken contours) found in the difference Fourier synthesis, computed at the conclusion of the refinement. Contour levels are at 0.1 e/$Å^3$ around the hydrogen atoms starting at the 0.6-electron level, for other atoms contour levels are at 1e/$Å^3$ except around Cl (2e/$Å^3$) starting at one electron level.

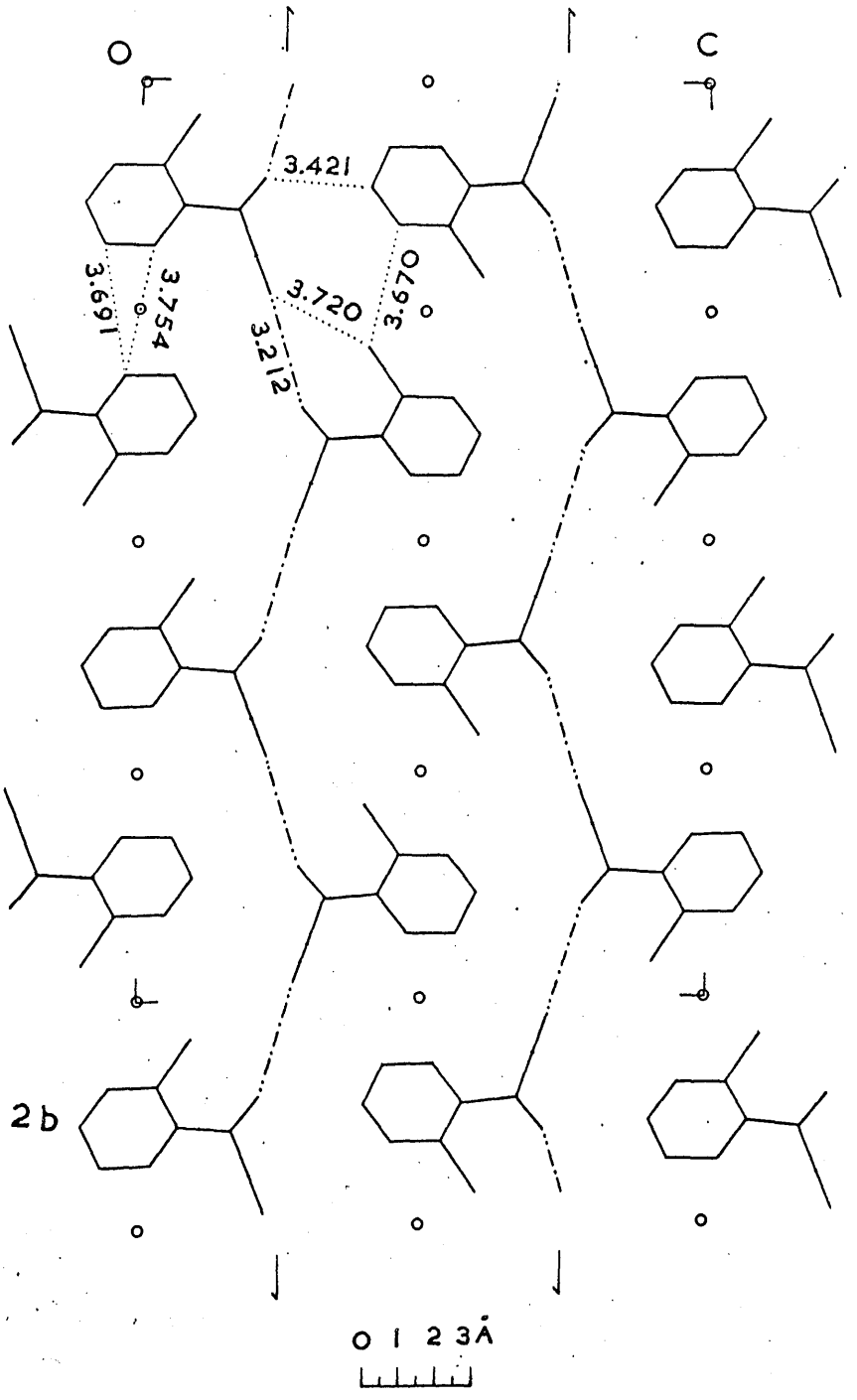


FIG. 1.5

The arrangement of the molecules viewed down the a-axis; intermolecular ≡C-H... bonds (.-.-.) and other short contacts (....).

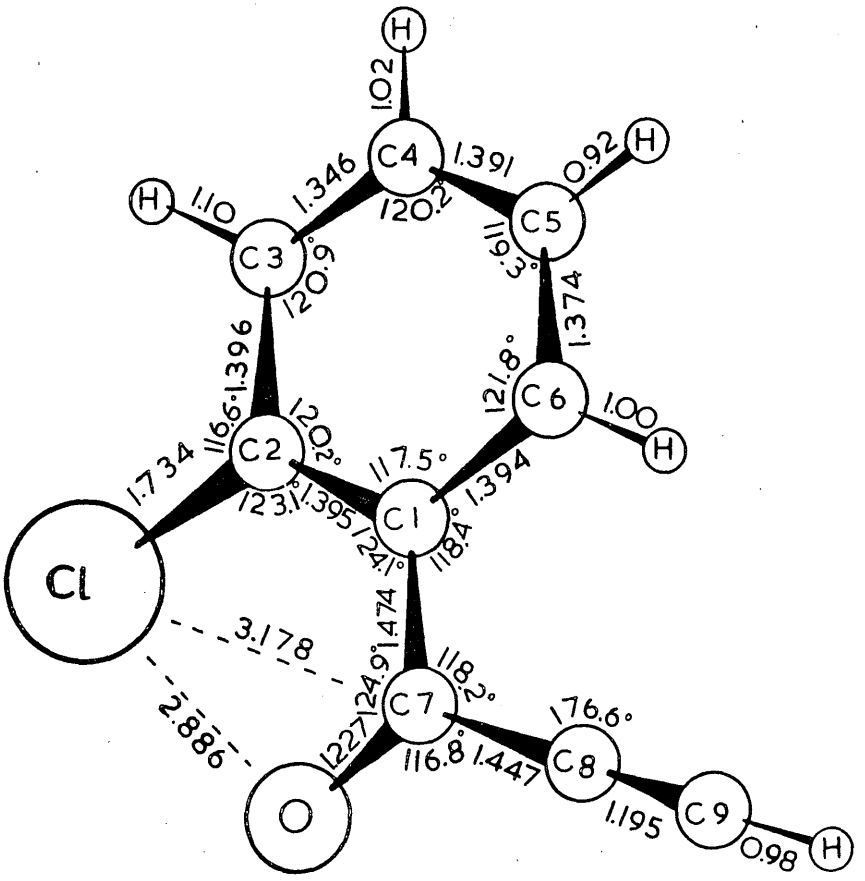


FIG. 1.6

The molecular diagram showing the intramolecular bonded distances (in Å), valency angles (in degrees) and the numbering scheme used for the non-hydrogen atoms (hydrogen atoms have the same numbers as the carbon atoms to which they are bonded). The C-H bond-lengths are based on the hydrogen positions obtained from the last difference synthesis.

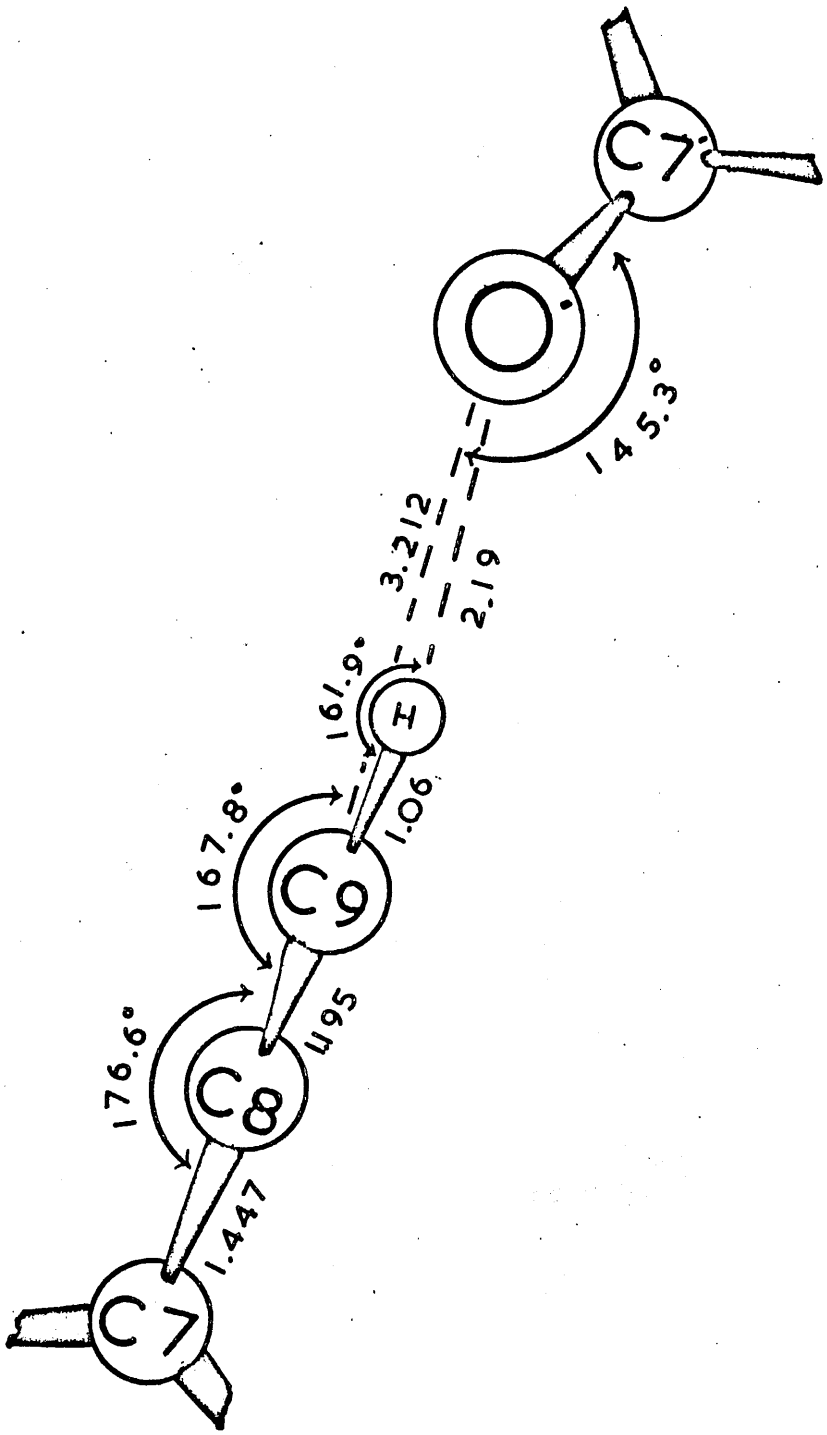


FIG. 1.7

Distances and angles associated with atoms involved in hydrogen bonding.

TABLE 1.1

COURSE OF THE STRUCTURE SOLUTION

Operation	Atoms found	R factor
1) Using 0kℓ data only		
a) Patterson projection	Cl	-
b) Minimum function	All non-hydrogen atoms	
c) Structure factor calculation		0.19
d) Refinement by least squares methods	-Do-	0.09
2) Using 0kℓ to 3kℓ data		
a) From Harker section at v=1/2 and inference from tilt of benzene ring	Cl,C(1) to C(7)	
b) Structure factor calculation		0.39
c) Calc. of electron density distribution	All non-H atoms	
d) Structure factor calculation		0.18

TABLE 1.2

PROGRESS OF THE LEAST SQUARES REFINEMENT

Cycle	R factor	$\Sigma \Delta w^2$	$R' = \Sigma w \Delta^2 / \Sigma w \lvert Fo \rvert^2$
1[a]	0.176	399	0.070
2	0.161	302	0.055
3	0.158	284	0.053
4[b]	0.158	283	0.052
5	0.124	181	0.034
6	0.116	156	0.030
7	0.113	145	0.028
8[c]	0.110	137	0.027
9[d]	0.096	111	0.022
10	0.094	67	0.017
11	0.093	67	0.017
12	0.092	67	0.017

a) Isotropic full matrix , b) anisotropic block diagonal and hydrogen atoms introduced , c) changes in weighting scheme , d) independent re-estimation of a few planes with bad agreements and changes in weighting scheme .

TABLE 1.3

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	|Fo|	Fc
0	0	2	32.1	37.0
0	0	4	0.6	-0.1
0	0	6	61.0	-64.3
0	0	8	26.0	-22.9
0	0	10	18.2	16.5
0	0	12	1.2	0.6
0	0	14	6.4	-5.8
0	0	16	13.6	-13.0
0	0	18	3.3	3.5
0	1	1	17.3	18.6
0	1	2	46.8	-47.8
0	1	3	0.5	-0.4
0	1	4	30.0	31.1
0	1	5	49.8	-55.2
0	1	6	28.5	-28.4
0	1	7	1.9	3.3
0	1	8	14.1	12.8
0	1	9	11.3	11.0
0	1	10	10.9	-10.4
0	1	11	10.0	10.4
0	1	12	5.2	-4.1
0	1	13	5.1	-4.9
0	1	14	10.0	-10.5
0	1	15	8.5	-7.5
0	1	16	1.3	-1.3
0	1	17	1.2	-1.7
0	1	18	1.0	-1.0
0	1	19	3.8	2.6
0	2	0	60.5	-60.7
0	2	1	12.0	-12.3
0	2	2	21.3	-20.8
0	2	3	47.3	-50.6
0	2	4	10.0	-10.5
0	2	5	3.4	-5.7
0	2	6	7.8	-8.0
0	2	7	39.8	39.6
0	2	8	23.0	22.0
0	2	9	14.0	13.4
0	2	10	12.6	11.7
0	2	11	1.2	0.9
0	2	12	1.2	-0.8
0	2	13	1.3	-2.1
0	2	14	1.3	-2.0
0	2	15	1.3	1.2
0	2	16	2.8	2.8
0	2	17	6.4	5.9
0	3	1	17.3	17.3
0	3	2	38.2	-40.1
0	3	3	7.9	-7.2
0	3	4	24.0	-24.8
0	3	5	19.9	-19.9
0	3	6	24.5	23.1
0	3	7	9.0	9.5
0	3	8	23.2	24.2
0	3	9	7.4	-8.1
0	3	10	6.8	-6.9
0	3	11	23.5	21.3
0	3	12	23.3	-21.8
0	3	13	1.3	1.2
0	3	14	2.9	-2.2
0	3	15	6.5	4.0
0	3	16	1.2	1.0
0	3	17	1.1	-1.2
0	3	18	7.5	6.7
0	4	0	1.4	-2.2
0	4	1	3.1	-3.8
0	4	2	32.7	-33.7
0	4	3	59.3	-60.6
0	4	4	4.1	-4.2
0	4	5	16.9	17.1
0	4	6	10.5	-8.2
0	4	7	13.0	11.5
0	4	8	4.3	3.7
0	4	9	13.1	12.0
0	4	10	1.2	-2.5
0	4	11	1.2	0.7
0	4	12	11.2	9.7
0	4	13	16.2	-15.1
0	4	14	2.9	2.7
0	4	15	1.3	1.2
0	4	16	6.0	-4.1
0	4	17	1.1	0.3
0	4	18	4.6	3.3
0	5	1	9.3	-8.5
0	5	2	34.2	-33.2
0	5	3	22.5	21.6
0	5	4	14.8	-14.4
0	5	5	47.6	45.3
0	5	6	1.0	1.1
0	5	7	7.7	-7.7
0	5	8	21.5	19.9
0	5	9	6.7	-6.2
0	5	10	8.0	8.0
0	5	11	24.2	-23.6
0	5	12	8.7	7.8
0	5	13	6.4	-6.8
0	5	14	4.1	-3.3
0	5	15	6.8	6.1
0	5	16	6.8	4.8
0	6	0	29.6	-27.9
0	6	1	11.3	-12.1
0	6	2	8.1	7.0
0	6	3	5.7	6.1
0	6	4	40.6	38.9
0	6	5	6.4	-5.2
0	6	6	21.0	23.4
0	6	7	5.4	6.5
0	6	8	5.7	-6.1
0	6	9	1.2	0.2
0	6	10	24.2	-22.4
0	6	11	21.2	-20.2
0	6	12	13.6	-12.6
0	6	13	2.9	-2.2
0	6	14	3.6	3.9
0	6	15	5.1	-4.4
0	6	16	5.4	3.8
0	7	1	27.5	-28.1
0	7	2	6.1	4.9
0	7	3	4.4	-3.9
0	7	4	1.1	0.9
0	7	5	4.7	4.3
0	7	6	1.1	-0.7
0	7	7	14.7	15.1
0	7	8	1.2	0.4
0	7	9	17.4	-17.2
0	7	10	5.8	-5.1
0	7	11	5.3	4.9
0	7	12	3.2	3.7
0	7	13	3.6	3.8
0	7	14	3.7	-3.7
0	7	15	2.5	2.0
0	7	16	3.1	2.4
0	8	0	18.0	-18.1
0	8	1	11.8	12.3
0	8	2	7.9	-7.0
0	8	3	1.1	-1.4
0	8	4	7.6	6.8
0	8	5	7.4	7.1
0	8	6	11.9	11.9
0	8	7	18.3	-17.5
0	8	8	3.1	-3.6
0	8	9	4.1	4.1
0	8	10	1.3	0.5
0	8	11	14.6	13.2
0	8	12	1.3	0.7
0	8	13	5.2	4.1
0	8	14	5.5	5.2
0	8	15	4.4	3.3
0	8	16	4.3	2.7
0	8	17	6.9	-5.0
0	9	1	19.4	-18.6
0	9	2	21.8	20.0
0	9	3	5.4	4.7
0	9	4	10.8	10.3
0	9	5	10.0	8.5
0	9	6	7.8	-7.4
0	9	7	4.3	3.8
0	9	8	12.1	-11.2
0	9	9	4.4	4.2
0	9	10	4.3	-4.1
0	9	11	10.0	-8.9
0	9	12	3.2	3.1
0	9	13	3.4	3.5
0	9	14	1.0	1.0
0	9	15	2.0	2.0
0	9	16	3.2	-2.7
0	10	0	5.5	4.7
0	10	1	15.0	15.1
0	10	2	6.4	-6.0
0	10	3	16.5	15.6
0	10	4	1.3	0.4
0	10	5	1.3	0.9
0	10	6	3.2	2.0
0	10	7	4.7	-4.9
0	10	8	3.2	-3.6
0	10	9	9.0	-7.9
0	10	10	1.2	0.5
0	10	11	2.9	3.2
0	10	12	4.6	-3.9
0	10	13	7.0	6.1
0	10	14	0.9	0.3
0	10	15	2.4	2.2
0	11	1	20.7	21.0
0	11	2	4.2	3.7
0	11	3	3.5	2.7
0	11	4	13.4	12.6
0	11	5	5.1	-5.6
0	11	6	12.6	-12.2
0	11	7	4.3	-5.4
0	11	8	3.1	-2.6
0	11	9	1.2	-2.1
0	11	10	1.2	-1.9
0	11	11	1.1	1.3
0	11	12	6.2	5.7
0	12	0	1.3	-0.6
0	12	1	4.9	5.1
0	12	2	9.4	8.9
0	12	3	1.3	2.3
0	12	4	12.8	-10.4
0	12	5	1.3	0.6
0	12	6	5.8	-4.8
0	12	7	8.5	-6.7
0	12	8	3.6	3.2
0	12	9	5.4	-4.7
0	12	10	4.3	4.6
0	13	1	1.2	-0.2
0	13	2	3.0	3.4
0	13	3	5.9	-6.2
0	13	4	1.2	-0.9
0	13	5	4.3	-4.1
0	13	6	1.1	1.8
0	13	7	1.0	-1.0
0	13	8	1.0	-0.2
0	13	9	9.7	7.6
0	13	10	0.8	0.4
0	13	11	2.5	2.4
0	14	0	11.8	9.0
0	14	1	1.1	-0.9
0	14	2	2.6	2.5
0	14	3	1.0	-1.6
0	14	4	7.1	-5.6
0	14	5	1.0	0.9
0	14	6	4.6	-4.2
0	14	7	2.9	2.2
0	15	1	4.6	3.7
0	15	2	7.4	-5.1
0	15	3	3.1	-2.9
0	15	4	1.7	-1.4
0	15	5	4.4	-3.5
0	15	6	1.9	1.8
1	0	14	7.4	-7.6
1	0	12	11.0	11.2
1	0	10	4.2	-3.4
1	0	8	21.9	-22.9
1	0	6	61.2	-66.0
1	0	4	1.9	2.2
1	0	2	67.2	66.5
1	0	-2	95.3	97.4
1	0	-4	61.8	-62.2
1	1	14	11.9	-12.1
1	1	13	8.8	8.9
1	1	12	3.6	-4.2
1	1	11	8.3	9.1
1	1	10	3.3	0.9
1	1	9	3.1	3.2
1	1	8	2.9	2.0
1	1	7	21.1	-22.3
1	1	6	16.0	-16.0
1	1	5	2.2	-0.4
1	1	4	42.0	-40.8
1	1	3	20.2	18.0
1	1	2	39.4	38.5
1	1	1	38.2	35.6
1	1	0	18.3	-16.7
1	1	-1	12.8	-12.4
1	1	-2	41.8	40.2
1	1	-3	58.6	-61.0
1	1	-4	14.6	-15.0
1	1	-5	11.6	10.1
1	1	-6	20.7	-20.5
1	1	-7	2.4	0.4
1	1	-8	16.1	14.5
1	2	14	9.0	8.2
1	2	13	3.7	-4.9
1	2	12	3.7	3.0
1	2	11	5.9	5.9
1	2	10	3.3	3.2
1	2	9	8.7	8.2
1	2	8	14.5	-14.1
1	2	7	3.0	-3.0
1	2	6	17.2	16.7
1	2	5	28.3	-28.6
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1	2	3	8.3	-9.5
1	2	2	53.1	56.7
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1	2	-3	26.3	26.7
1	2	-4	24.1	-23.0
1	2	-5	5.9	-5.2
1	2	-6	9.1	7.9
1	2	-7	14.0	-14.3
1	2	-8	30.2	31.3
1	3	9	15.3	-14.4
1	3	10	10.4	9.6
1	3	9	3.2	3.6
1	3	8	8.1	8.8
1	3	7	16.0	-17.2
1	3	6	2.6	1.7
1	3	5	2.4	0.5
1	3	4	31.9	-34.2
1	3	3	5.4	-4.6
1	3	2	19.1	-19.7
1	3	1	11.1	10.4
1	3	0	41.3	41.2
1	3	-1	10.7	10.0
1	3	-2	8.6	-6.6
1	3	-3	1.9	-0.8
1	3	-4	12.4	-12.9
1	3	-5	24.3	-22.3
1	3	-6	44.3	-46.4
1	3	-7	2.6	1.7
1	3	-8	2.8	1.3
1	3	-9	8.3	7.7
1	3	-10	14.5	14.0
1	4	11	6.1	6.1
1	4	10	16.5	15.9
1	4	9	31.2	33.2
1	4	8	10.2	9.8
1	4	7	3.0	0.4
1	4	6	9.5	8.9
1	4	5	22.4	-23.1
1	4	4	15.9	-15.9
1	4	3	25.7	-25.4
1	4	2	32.9	-33.2
1	4	1	11.5	-9.8
1	4	0	2.1	-1.2
1	4	-1	20.0	22.2
1	4	-2	20.4	20.6
1	4	-3	18.8	-17.9
1	4	-4	4.8	-4.3
1	4	-5	22.5	-23.5
1	4	-6	9.9	-10.2
1	4	-7	27.0	-28.2
1	4	-8	21.9	-19.9
1	4	-9	22.1	22.2
1	4	-10	3.3	-1.0
1	4	-11	11.2	10.6
1	5	11	22.3	-23.6
1	5	10	22.0	21.5
1	5	9	3.5	-3.7
1	5	8	12.7	12.5
1	5	7	16.9	15.4
1	5	6	8.2	-8.5
1	5	5	2.8	-1.3
1	5	4	20.8	-21.5
1	5	3	14.3	12.6
1	5	2	2.4	-0.8
1	5	1	24.0	-22.3
1	5	0	19.1	20.8
1	5	-1	17.3	19.3
1	5	-2	26.1	25.6
1	5	-3	16.7	16.7
1	5	-4	2.5	-2.3
1	5	-5	26.5	28.3
1	5	-6	13.3	-13.8
1	5	-7	9.9	-9.5
1	5	-8	3.1	-1.0
1	5	-9	11.4	-11.0
1	6	13	6.0	-5.7
1	6	12	12.1	-12.8
1	6	11	3.7	2.2
1	6	10	14.7	-15.0
1	6	9	19.9	-20.2
1	6	8	3.5	1.9
1	6	7	11.5	12.2
1	6	6	19.6	19.6
1	6	5	17.0	-17.0
1	6	4	2.9	1.5
1	6	3	2.8	1.8
1	6	2	9.9	-8.8
1	6	1	2.7	2.2
1	6	0	5.7	-6.7
1	6	-1	7.6	7.6
1	6	-2	18.9	19.7
1	6	-3	2.7	-1.4
1	6	-4	29.9	32.3
1	6	-5	13.8	-15.3
1	6	-6	3.0	4.2
1	6	-7	3.2	0.5
1	6	-8	13.5	-13.9
1	6	-9	4.4	-5.8
1	6	-10	6.0	-6.2
1	6	-11	12.5	12.8
1	7	13	6.1	-6.8
1	7	12	7.6	-8.3
1	7	11	5.7	5.3
1	7	10	3.7	-5.1
1	7	9	13.2	12.9
1	7	8	11.2	-9.7
1	7	7	12.5	11.7
1	7	6	3.4	1.8
1	7	5	12.1	13.0
1	7	4	10.0	8.8
1	7	3	36.3	-37.2
1	7	2	3.0	1.8
1	7	1	24.9	-22.4
1	7	0	5.9	6.1
1	7	-1	2.9	-2.6
1	7	-2	5.6	5.6
1	7	-3	26.8	27.9
1	7	-4	9.7	9.3
1	7	-5	3.2	-4.0
1	7	-6	7.1	6.5
1	7	-7	11.5	-11.5
1	7	-8	3.5	-3.3
1	7	-9	12.8	-13.1
1	8	7	11.2	10.6
1	8	6	8.5	7.6
1	8	5	7.9	6.4
1	8	4	7.1	-5.7
1	8	3	11.9	11.3
1	8	2	16.8	-17.0
1	8	1	8.2	-8.4
1	8	0	10.7	-10.6
1	8	-1	8.8	-8.0
1	8	-2	11.7	13.1
1	8	-3	7.1	7.5
1	8	-4	11.1	10.6
1	8	-5	18.8	20.1
1	8	-6	3.5	-5.2
1	8	-7	3.6	2.3
1	8	-8	6.9	-7.0
1	8	-9	3.7	2.8
1	8	-10	3.7	-3.5
1	8	-11	15.7	-16.9
1	8	-12	12.7	13.9
1	9	8	6.6	-6.4
1	9	7	10.8	9.3
1	9	6	9.6	9.4
1	9	5	6.1	6.3
1	9	4	10.4	11.6
1	9	3	3.6	-1.9
1	9	2	5.0	-5.8
1	9	1	8.5	-7.5
1	9	0	19.3	-17.7
1	9	-1	19.0	-19.8
1	9	-2	23.2	-25.9
1	9	-3	3.5	-3.1
1	9	-4	2.5	2.0
1	9	-5	13.0	13.1
1	9	-6	9.4	-9.4
1	9	-7	5.1	4.8
1	9	-8	3.7	2.2
1	9	-9	4.7	-4.7
1	9	-10	12.7	12.5
1	9	-11	7.8	7.4
1	10	3	12.8	12.4
1	10	2	3.7	-3.3
1	10	1	9.8	-9.5
1	10	0	3.7	-2.5
1	10	-1	10.3	-9.6
1	10	-2	3.7	1.4
1	10	-3	10.6	-11.4
1	10	-4	3.7	-2.5
1	10	-5	11.5	10.4
1	10	-6	3.7	4.7
1	10	-7	7.4	7.1
1	10	-8	3.7	-0.7
1	10	-9	6.9	-8.1
1	11	7	9.4	-9.7
1	11	6	5.6	5.4
1	11	5	5.2	-5.2
1	11	4	3.7	3.6
1	11	3	4.1	4.0
1	11	2	7.1	8.2
1	11	1	11.5	12.1
1	11	0	13.7	-15.5
1	11	-1	10.2	9.4
1	11	-2	3.7	-2.5
1	11	-3	3.7	4.1
1	11	-4	7.0	7.3
1	11	-5	3.7	-4.2
1	11	-6	6.1	6.2
1	11	-7	3.6	4.4
1	11	-8	5.9	5.4
1	11	-9	3.4	-2.1
1	11	-10	6.5	-7.4
1	12	2	8.8	8.5
1	12	1	5.6	-5.2
1	12	0	5.1	5.1
1	12	-1	3.6	-4.1
1	12	-2	12.4	-12.8
1	12	-3	3.6	-1.9
1	12	-4	3.6	-2.3
1	12	-5	3.5	5.6
1	12	-6	3.4	-2.2
1	12	-7	3.3	4.6
1	12	-8	6.1	7.0
1	13	3	7.1	7.1
1	13	2	3.3	1.7
1	13	1	3.3	2.7
1	13	0	7.6	7.7
1	13	-1	7.9	-8.7
1	13	-2	3.3	-0.8
1	13	-3	9.3	-10.4
1	13	-4	3.2	2.8
1	13	-5	3.4	-4.6
1	13	-6	3.0	3.0
1	13	-7	7.3	8.2
2	0	10	7.3	-7.6
2	0	8	10.1	-10.3
2	0	6	5.3	-4.9
2	0	4	11.0	10.6
2	0	2	14.3	12.6
2	0	-2	10.2	-14.6
2	0	-4	14.6	13.2
2	0	-6	3.2	1.6
2	0	-8	4.7	6.1
2	0	-10	6.8	-6.3
2	0	-12	9.5	-9.1
2	1	16	3.8	-4.7
2	1	15	2.2	3.6
2	1	14	2.5	-1.3
2	1	13	6.5	7.0
2	1	12	2.7	-3.8
2	1	11	2.7	3.2
2	1	10	4.8	5.1
2	1	9	9.8	-9.8
2	1	8	6.8	-6.3
2	1	7	2.3	-1.7
2	1	6	5.7	-5.1
2	1	5	13.1	12.7
2	1	4	17.7	-17.4
2	1	3	31.0	29.0
2	1	2	14.0	14.0
2	1	1	5.6	-4.1
2	1	0	12.9	16.5
2	1	-1	21.1	-25.5
2	1	-2	12.4	-15.5
2	1	-3	12.8	-11.4
2	1	-4	1.3	1.4
2	1	-5	8.7	7.6
2	1	-6	1.7	-1.1
2	1	-7	31.1	31.3
2	1	-8	9.4	9.2
2	1	-9	10.2	-10.1
2	1	-10	8.5	8.4
2	1	-11	5.8	-6.6
2	1	-12	7.5	-6.9
2	1	-13	12.2	-12.2
2	2	14	4.4	5.9
2	2	13	2.6	1.6
2	2	12	4.9	5.4
2	2	11	2.7	4.3
2	2	10	9.5	-10.1
2	2	9	8.9	-8.6
2	2	8	14.6	-15.2
2	2	7	23.4	-23.0
2	2	6	2.2	0.2
2	2	5	23.9	-22.6
2	2	4	32.0	30.6
2	2	3	8.2	8.0
2	2	2	6.9	4.8
2	2	1	44.6	42.7
2	2	0	14.2	11.5
2	2	-1	27.8	26.0

TABLE 1.3 Cont.

H	K	L	|Fo|	Fo
2	2	-2	54.6	-53.5
2	2	-3	25.9	24.5
2	2	-4	6.8	-5.2
2	2	-5	11.0	-9.6
2	2	-6	16.8	16.7
2	2	-7	18.4	18.3
2	2	-8	15.7	15.4
2	2	-9	10.1	9.3
2	2	-10	2.4	1.9
2	2	-11	5.6	-5.8
2	2	-12	6.8	-6.3
2	3	12	7.2	8.1
2	3	11	2.7	-3.3
2	3	10	9.3	9.6
2	3	9	5.0	-4.6
2	3	8	4.3	-4.7
2	3	7	10.4	-8.9
2	3	6	19.4	-18.3
2	3	5	5.4	-3.9
2	3	4	12.9	12.2
2	3	3	6.4	-4.3
2	3	2	8.9	6.8
2	3	1	7.6	5.8
2	3	0	18.7	16.8
2	3	-1	7.8	-7.9
2	3	-2	18.1	-17.1
2	3	-3	9.7	8.4
2	3	-4	43.7	-45.2
2	3	-5	4.1	-3.4
2	3	-6	4.4	-3.4
2	3	-7	5.9	-5.8
2	3	-8	2.2	2.6
2	3	-9	6.4	6.1
2	3	-10	14.4	14.7
2	3	-11	2.6	-0.8
2	3	-12	2.7	-2.8
2	3	-13	4.9	6.0
2	3	-14	2.7	2.1
2	3	-15	6.8	7.4
2	4	16	3.0	-2.8
2	4	15	6.9	-7.1
2	4	14	2.3	-1.2
2	4	13	6.1	6.3
2	4	12	2.7	-0.8
2	4	11	8.5	8.8
2	4	10	9.3	9.7
2	4	9	13.0	13.7
2	4	8	19.5	20.8
2	4	7	2.5	1.3
2	4	6	6.6	-7.2
2	4	5	12.5	-11.9
2	4	4	7.6	-6.1
2	4	3	6.3	6.5
2	4	2	13.8	-13.5
2	4	1	14.2	13.5
2	4	0	1.7	1.2
2	4	-1	16.5	-15.8
2	4	-2	33.2	32.1
2	4	-3	38.4	-39.8
2	4	-4	6.5	5.9
2	4	-5	24.0	-24.9
2	4	-6	4.6	-3.6
2	4	-7	2.2	-2.2
2	4	-8	9.4	-10.1
2	4	-9	16.9	17.6
2	4	-10	2.6	-3.9
2	4	-11	9.9	10.4
2	4	-12	2.7	-2.0
2	5	13	4.9	-5.1
2	5	12	4.8	-3.9
2	5	11	1.8	-0.9
2	5	10	2.2	-3.2
2	5	9	4.8	-5.0
2	5	8	6.1	6.9
2	5	7	6.6	7.0
2	5	6	5.2	5.1
2	5	5	5.7	-6.3
2	5	4	2.7	3.0
2	5	3	11.5	11.4
2	5	2	11.8	-11.5
2	5	1	11.1	-11.1
2	5	0	18.1	18.5
2	5	-1	12.2	10.9
2	5	-2	13.3	13.0
2	5	-3	8.3	8.1
2	5	-4	3.7	4.1
2	5	-5	2.0	1.3
2	5	-6	10.6	-11.2
2	5	-7	13.3	-14.1
2	5	-8	2.2	-3.1
2	5	-9	4.4	-5.0
2	5	-10	4.9	4.6
2	6	14	2.0	-1.7
2	6	13	2.3	-2.4
2	6	12	2.5	-3.4
2	6	11	2.6	2.8
2	6	10	2.7	1.1
2	6	9	2.7	0.8
2	6	8	4.9	5.1
2	6	7	14.8	-16.2
2	6	6	2.6	-3.3
2	6	5	7.3	6.6
2	6	4	11.4	-10.4
2	6	3	10.0	-9.9
2	6	2	7.4	-6.5
2	6	1	12.4	12.2
2	6	0	14.8	15.1
2	6	-1	2.2	2.8
2	6	-2	10.5	9.6
2	6	-3	2.2	0.4
2	6	-4	7.9	-7.5
2	6	-5	11.9	-11.7
2	6	-6	12.8	-13.8
2	6	-7	2.5	-1.0
2	6	-8	4.6	-4.9
2	6	-9	2.7	0.2
2	6	-10	7.7	7.8
2	6	-11	2.7	-1.3
2	6	-12	9.1	9.3
2	7	15	2.9	-2.1
2	7	14	1.7	-1.7
2	7	13	2.1	-2.9
2	7	12	2.3	-0.4
2	7	11	2.5	1.7
2	7	10	9.7	-10.2
2	7	9	19.3	21.6
2	7	8	2.7	-3.6
2	7	7	7.3	7.7
2	7	6	2.7	-3.2
2	7	5	9.5	-9.8
2	7	4	2.6	-2.5
2	7	3	17.7	-17.8
2	7	2	5.0	4.7
2	7	1	7.1	-7.2
2	7	0	2.4	1.3
2	7	-1	20.3	19.7
2	7	-2	15.8	15.7
2	7	-3	17.7	18.6
2	7	-4	9.0	8.9
2	7	-5	5.3	-4.5
2	7	-6	2.6	3.4
2	7	-7	16.3	-18.2
2	8	14	3.2	-3.7
2	8	13	1.8	-0.8
2	8	12	5.3	-5.3
2	8	11	6.4	-7.0
2	8	10	2.5	3.1
2	8	9	2.6	2.2
2	8	8	2.7	2.2
2	8	7	6.5	5.9
2	8	6	2.7	1.0
2	8	5	2.7	4.0
2	8	4	14.8	-15.1
2	8	3	5.6	-6.1
2	8	2	11.3	-11.4
2	8	1	5.7	-5.6
2	8	0	9.2	6.4
2	8	-1	2.6	1.5
2	8	-2	10.3	10.1
2	8	-3	11.1	10.1
2	8	-4	6.2	5.9
2	8	-5	14.3	17.0
2	8	-6	11.8	-13.0
2	8	-7	2.7	-3.3
2	8	-8	6.7	-6.3
2	8	-9	2.7	-2.8
2	8	-10	4.5	4.4
2	8	-11	2.7	0.6
2	8	-12	6.2	7.1
2	8	-13	2.4	-3.0
2	8	-14	6.3	7.3
2	9	8	10.2	11.0
2	9	7	2.7	2.8
2	9	6	9.5	10.7
2	9	5	2.7	-1.8
2	9	4	5.4	5.6
2	9	3	2.7	1.8
2	9	2	16.4	-16.3
2	9	1	2.7	-2.1
2	9	0	16.9	-17.4
2	9	-1	6.8	7.4
2	9	-2	2.7	-3.0
2	9	-3	2.7	-4.0
2	9	-4	2.7	-1.7
2	9	-5	2.7	-2.0
2	9	-6	2.7	-0.7
2	9	-7	2.7	2.2
2	9	-8	10.0	-10.6
2	9	-9	2.7	-3.9
2	9	-10	2.6	-0.7
2	9	-11	5.9	6.7
2	9	-12	2.3	2.4
2	9	-13	2.2	-0.2
2	9	-14	6.4	7.9
2	10	7	4.7	5.8
2	10	6	4.9	5.2
2	10	5	9.5	10.1
2	10	4	2.7	-1.0
2	10	3	2.7	-3.5
2	10	2	2.7	3.8
2	10	1	9.5	-9.3
2	10	0	4.9	-5.0
2	10	-1	5.2	-6.0
2	10	-2	2.7	2.4
2	10	-3	10.7	11.4
2	10	-4	2.7	4.2
2	10	-5	2.7	-0.3
2	10	-6	2.7	2.0
2	10	-7	2.7	-0.9
2	10	-8	2.6	2.0
2	10	-9	7.5	-8.8
2	10	-10	2.4	-2.4
2	10	-11	2.3	-2.0
2	10	-12	3.9	-4.6
2	11	8	2.1	0.4
2	11	7	2.2	-2.0
2	11	6	6.0	6.1
2	11	5	2.5	0.5
2	11	4	2.5	1.7
2	11	3	2.6	2.1
2	11	2	5.5	-6.2
2	11	1	3.7	-3.8
2	11	0	4.8	-4.6
2	11	-1	2.7	-3.1
2	11	-2	2.7	0.3
2	11	-3	2.7	2.5
2	11	-4	9.7	11.4
2	11	-5	2.6	3.2
2	11	-6	5.8	5.5
2	11	-7	2.5	-1.6
2	11	-8	4.8	-5.2
2	11	-9	2.3	-0.9
2	11	-10	2.2	-2.8
2	11	-11	2.0	-4.2
2	12	8	4.2	-4.1
2	12	7	3.3	3.3
2	12	6	2.0	2.5
2	12	5	2.2	1.6
2	12	4	7.3	7.1
2	12	3	2.3	-1.3
2	12	2	2.4	1.8
2	12	1	2.4	-3.6
2	12	0	2.5	-2.9
2	12	-1	4.7	-5.4
2	12	-2	6.2	-7.4
2	12	-3	4.6	5.1
2	12	-4	2.4	-1.5
2	12	-5	4.7	5.5
2	12	-6	7.2	6.2
2	12	-7	2.2	1.1
2	12	-8	2.1	0.8
2	12	-9	1.9	-1.5
2	12	-10	1.7	-2.6
2	12	-11	4.4	-4.1
2	13	6	2.7	-3.4
2	13	5	5.1	4.9
2	13	4	1.9	3.3
2	13	3	5.3	5.4
2	13	2	2.0	-0.2
2	13	1	2.1	0.6
2	13	0	2.1	2.7
2	13	-1	8.2	-8.7
2	13	-2	4.7	5.0
2	13	-3	7.3	-7.1
2	13	-4	2.1	1.6
2	13	-5	5.2	5.2
2	13	-6	4.5	4.2
2	13	-7	5.5	4.8
2	13	-8	1.6	-0.2
2	13	-9	4.3	3.4
2	14	2	3.3	3.9
2	14	1	1.6	1.6
2	14	0	5.7	-5.8
2	14	-1	1.7	-1.1
2	14	-2	1.6	-1.3
2	14	-3	5.1	-4.8
2	14	-4	1.5	-1.2
2	14	-5	1.4	-2.0
2	14	-6	3.6	4.1
3	0	14	4.0	3.7
3	0	12	8.0	-8.0
3	0	10	2.0	-3.4
3	0	8	7.5	7.6
3	0	-4	9.0	10.3
3	0	-6	3.4	3.1
3	0	-8	18.2	-18.1
3	0	-10	13.2	-12.5
3	0	-12	2.0	2.4
3	0	-14	5.4	5.4
3	0	-16	11.2	12.2
3	1	9	2.0	-3.7
3	1	8	2.0	-0.8
3	1	7	7.1	7.5
3	1	6	1.9	2.3
3	1	5	13.7	13.1
3	1	4	7.3	5.4
3	1	3	1.5	2.7
3	1	2	1.4	0.7
3	1	1	11.6	-10.7
3	1	0	2.6	2.8
3	1	-1	8.0	-10.4
3	1	-2	7.2	-9.4
3	1	-3	6.4	8.5
3	1	-4	4.5	-1.5
3	1	-5	15.9	14.5
3	1	-6	10.5	10.6
3	1	-7	1.6	1.1
3	1	-8	9.6	8.6
3	1	-9	3.6	-3.7
3	1	-10	8.0	-2.5
3	1	-11	8.5	-9.4
3	1	-12	2.5	-2.6
3	1	-13	3.6	3.7
3	1	-14	9.1	-9.7
3	1	-15	1.8	1.2
3	1	-16	5.7	-6.2
3	2	10	4.7	-4.5
3	2	9	9.3	-10.0
3	2	8	9.5	-10.6
3	2	7	16.4	-17.9
3	2	6	2.0	-1.8
3	2	5	1.9	-2.1
3	2	4	10.1	8.7
3	2	3	9.2	7.1
3	2	2	1.5	0.9
3	2	1	11.9	10.1
3	2	0	3.9	-3.6
3	2	-1	3.1	-2.8
3	2	-2	5.0	4.3
3	2	-3	5.4	-4.0
3	2	-4	1.3	-2.2
3	2	-5	13.4	13.0
3	2	-6	11.7	10.1
3	2	-7	8.2	7.1
3	2	-8	4.4	4.6
3	2	-9	6.6	7.9
3	2	-10	2.0	-1.8
3	2	-11	5.7	-6.1
3	2	-12	4.2	-4.2
3	3	13	1.8	1.6
3	3	12	6.4	6.3
3	3	11	7.4	-7.4
3	3	10	1.9	-1.4
3	3	9	2.0	-2.3
3	3	8	5.0	-5.0
3	3	7	4.1	-3.9
3	3	6	6.6	-6.9
3	3	5	5.5	-3.9
3	3	4	13.8	13.5
3	3	3	1.7	-1.8
3	3	2	21.9	19.6
3	3	1	9.5	-7.8
3	3	0	15.6	-12.4
3	3	-1	1.4	1.5
3	3	-2	15.5	-13.0
3	3	-3	5.9	-3.2
3	3	-4	11.1	-11.3
3	3	-5	11.5	11.2
3	3	-6	3.7	3.6
3	3	-7	3.4	-2.7
3	3	-8	10.7	10.3
3	3	-9	2.0	-1.5
3	3	-10	5.7	-5.1
3	3	-11	2.0	-2.6
3	3	-12	5.4	-5.6
3	3	-13	2.0	-1.8
3	3	-14	1.9	-0.8
3	3	-15	1.7	2.6
3	3	-16	4.1	4.3
3	4	13	1.3	1.3
3	4	12	1.5	0.8
3	4	11	6.2	5.9
3	4	10	1.9	2.2
3	4	9	5.1	-5.2
3	4	8	2.0	2.9
3	4	7	2.0	1.9
3	4	6	4.8	4.4
3	4	5	7.1	6.8
3	4	4	12.9	-12.5
3	4	3	14.6	14.6
3	4	2	6.7	6.0
3	4	1	4.0	3.2
3	4	0	1.6	-0.8
3	4	-1	14.7	-14.3
3	4	-2	7.2	6.1
3	4	-3	28.6	-25.8
3	4	-4	14.7	14.2
3	4	-5	4.3	-4.9
3	4	-6	1.8	2.2
3	4	-7	11.0	10.3
3	4	-8	4.4	4.7
3	4	-9	2.0	2.6
3	4	-10	2.0	-2.4
3	4	-11	2.0	1.4
3	4	-12	4.0	-3.7
3	4	-13	5.2	-4.3
3	5	11	5.1	4.7
3	5	10	1.8	-0.4
3	5	9	7.7	6.6
3	5	8	7.0	-8.2
3	5	7	7.2	-7.9
3	5	6	2.0	-2.1
3	5	5	2.0	1.1
3	5	4	2.0	2.3
3	5	3	5.3	5.0
3	5	2	3.7	3.6
3	5	1	10.7	9.0
3	5	0	6.1	5.2
3	5	-1	7.1	6.0
3	5	-2	14.1	-12.5
3	5	-3	17.9	-17.0
3	5	-4	1.8	-0.7
3	5	-5	21.5	-19.7
3	5	-6	5.2	4.1
3	5	-7	2.0	-0.6
3	5	-8	7.4	7.2
3	5	-9	5.4	5.5
3	5	-10	2.0	1.2
3	5	-11	4.4	4.9
3	6	12	4.1	4.4
3	6	11	1.5	0.5
3	6	10	5.8	6.0
3	6	9	1.8	1.6
3	6	8	1.9	-1.0
3	6	7	2.0	-2.8
3	6	6	6.2	-5.9
3	6	5	5.5	-5.7
3	6	4	4.4	-3.9
3	6	3	9.3	9.3
3	6	2	11.3	10.6
3	6	1	1.9	-0.3
3	6	0	12.7	11.3
3	6	-1	1.9	1.3
3	6	-2	6.6	-5.9
3	6	-3	3.4	2.4
3	6	-4	22.2	-21.8
3	6	-5	2.0	-1.2
3	6	-6	13.6	-14.7
3	6	-7	2.0	1.8
3	6	-8	3.9	3.7
3	6	-9	2.0	1.5
3	6	-10	7.9	-7.9
3	6	-11	5.0	-5.2
3	6	-12	3.8	3.3
3	7	10	1.5	1.5
3	7	9	6.2	6.4
3	7	8	5.9	-5.0
3	7	7	1.9	1.3
3	7	6	2.0	-2.8
3	7	5	10.5	-11.5
3	7	4	2.0	-2.6
3	7	3	4.8	-4.9
3	7	2	2.0	-1.7
3	7	1	8.9	8.7
3	7	0	9.1	9.0
3	7	-1	9.1	8.8
3	7	-2	2.0	1.8
3	7	-3	4.0	3.3
3	7	-4	5.6	5.3
3	7	-5	2.0	1.3
3	7	-6	2.0	-1.5
3	7	-7	2.0	-1.0
3	7	-8	2.0	0.8
3	7	-9	5.8	5.1
3	7	-10	2.0	2.1
3	7	-11	1.9	2.1
3	7	-12	1.8	-1.4
3	7	-13	4.8	-4.9
3	8	7	5.7	6.5
3	8	6	9.5	-9.8
3	8	5	4.9	-4.9
3	8	4	5.3	-5.7
3	8	3	5.6	-5.0
3	8	2	2.0	-2.6
3	8	1	2.0	-2.9
3	8	0	7.2	7.1
3	8	-1	8.0	7.7
3	8	-2	6.1	5.6
3	8	-3	2.0	2.4
3	8	-4	5.5	-5.3
3	8	-5	2.0	-2.0
3	8	-6	2.0	-1.8
3	8	-7	2.0	-0.4
3	8	-8	2.0	-1.1
3	8	-9	1.9	-2.1
3	8	-10	4.5	4.7
3	8	-11	6.1	6.3
3	9	8	8.5	9.3
3	9	7	5.8	-5.6
3	9	6	6.0	6.2
3	9	5	1.8	-2.9
3	9	4	3.9	-3.8
3	9	3	1.9	-1.6
3	9	2	5.6	-6.3
3	9	1	7.6	8.3
3	9	0	2.0	-2.4
3	9	-1	4.0	3.9
3	9	-2	4.7	4.2
3	9	-3	2.0	1.8
3	9	-4	2.0	-1.2
3	9	-5	7.5	-8.5
3	9	-6	7.9	-9.3
3	9	-7	2.0	1.7
3	9	-8	5.1	-5.6
3	9	-9	4.8	4.3
3	10	8	3.1	3.7
3	10	7	1.3	1.8
3	10	6	1.5	1.6
3	10	5	1.6	-2.5
3	10	4	1.7	0.4
3	10	3	6.0	-6.4
3	10	2	1.8	-0.9
3	10	1	4.4	-3.4
3	10	0	1.9	1.5
3	10	-1	5.9	5.6
3	10	-2	1.9	1.8
3	10	-3	6.3	6.9
3	10	-4	1.9	2.1
3	10	-5	1.8	-1.3
3	10	-6	1.8	-2.9
3	10	-7	9.8	-9.7
3	11	2	5.1	-4.8
3	11	1	5.9	-5.2
3	11	0	1.7	1.8
3	11	-1	6.1	-5.4
3	11	-2	6.0	6.1
3	11	-3	1.9	1.3
3	11	-4	4.3	3.6
3	11	-5	1.6	1.4
3	11	-6	1.6	-1.3
3	11	-7	5.3	-5.4
3	11	-8	1.4	-2.0
3	11	-9	3.4	-4.8
3	11	-10	3.9	-1.6
3	11	-11	3.6	-3.8
3	12	-1	1.4	2.0
3	12	-2	1.4	1.2
3	12	-3	1.4	1.8
3	12	-4	3.3	2.9
3	12	-5	3.5	4.2

TABLE 1.4

FRACTIONAL COORDINATES AND E.S.D.S.

ATOM	x/a	y/b	z/c
Cl	-0.1763 ± 4	0.0756 ± 1	0.0990 ± 1
O	0.2402 ± 14	0.2103 ± 3	0.2213 ± 3
C(1)	0.1105 ± 13	0.2752 ± 4	0.0778 ± 3
C(2)	-0.0687 ± 13	0.1859 ± 4	0.0408 ± 4
C(3)	-0.1872 ± 15	0.1848 ± 5	-0.0465 ± 4
C(4)	-0.1226 ± 16	0.2678 ± 6	-0.0967 ± 4
C(5)	0.0630 ± 16	0.3568 ± 5	-0.0620 ± 4
C(6)	0.1721 ± 14	0.3601 ± 5	0.0243 ± 4
C(7)	0.2491 ± 13	0.2830 ± 4	0.1690 ± 3
C(8)	0.3961 ± 14	0.3849 ± 5	0.2008 ± 4
C(9)	0.5336 ± 18	0.4666 ± 5	0.2275 ± 4

TABLE 1.5

FRACTIONAL CO-ORDINATES OF THE HYDROGEN ATOMS OBTAINED FROM THE LAST DIFFERENCE SYNTHESIS

	x/a	y/b	z/c
H(C3)	-0.333	0.116	-0.074
H(C4)	-0.215	0.265	-0.164
H(C5)	0.121	0.423	-0.103
H(C6)	0.310	0.431	0.051
H(C9)	0.656	0.539	0.251

TABLE 1.6

ORTHOGONALISED COORDINATES AND E.S.D.S.(in Å) referred TO THE AXES PARALLEL TO a*,b and c

ATOM	X	Y	Z
Cl	-0.692 ± 2	0.934 ± 1	1.673 ± 2
O	0.943 ± 5	2.598 ± 4	3.372 ± 4
C(1)	0.434 ± 5	3.399 ± 5	1.171 ± 5
C(2)	-0.270 ± 5	2.297 ± 5	0.687 ± 6
C(3)	-0.735 ± 6	2.283 ± 6	-0.630 ± 6
C(4)	-0.481 ± 6	3.308 ± 7	-1.464 ± 6
C(5)	0.247 ± 6	4.408 ± 6	-1.020 ± 6
C(6)	0.675 ± 6	4.448 ± 6	0.285 ± 6
C(7)	0.978 ± 5	3.496 ± 5	2.537 ± 5
C(8)	1.554 ± 5	4.755 ± 6	2.956 ± 6
C(9)	2.094 ± 7	5.763 ± 7	3.301 ± 7

TABLE 1.7

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.
$o2$
(in A)

ATOM	U11	U22	U33	2U23	2U31	2U12
Cl	0.0563 11	0.0529 8	0.0798 12	0.0063 14	0.0083 15	-0.0216 12
O	0.1133 38	0.0570 24	0.0472 26	0.0132 40	-0.0014 49	-0.0165 48
C(1)	0.0350 30	0.0470 26	0.0442 30	-0.0139 44	0.0083 41	0.0196 40
C(2)	0.0311 31	0.0472 26	0.0605 36	0.0014 48	0.0122 45	0.0189 40
C(3)	0.0460 36	0.0689 36	0.0581 38	-0.0333 59	-0.0048 51	0.0265 53
C(4)	0.0546 39	0.0906 45	0.0409 34	-0.0082 61	-0.0038 51	0.0269 62
C(5)	0.0615 40	0.0680 36	0.0460 34	0.0128 56	0.0164 53	0.0181 56
C(6)	0.0492 36	0.0563 30	0.0484 33	0.0132 51	0.0205 49	0.0045 47
C(7)	0.0442 33	0.0552 29	0.0363 29	-0.0065 45	0.0091 42	0.0153 44
C(8)	0.0435 34	0.0590 31	0.0466 33	-0.0075 50	0.0014 47	0.0158 47
C(9)	0.0786 48	0.0654 38	0.0651 44	-0.0432 65	-0.0060 67	-0.0369 66

TABLE 1.8

PRINCIPAL VALUES AND DIRECTION COSINES OF VIBRATION TENSORS REFERRED TO THE ORTHOGONAL AXES PARALLEL TO a* , b and c

ATOM	U / A^2	D1	D2	D3
C1	0.0837	-0.2327	0.2283	0.9454
	0.0436	-0.6439	-0.7647	0.0262
	0.0634	0.7289	-0.6026	0.3249
O	0.1195	-0.9522	0.1587	0.2611
	0.0438	0.1735	-0.4225	0.8896
	0.0580	0.2515	0.8923	0.3748
C(1)	0.0575	-0.3571	-0.7658	0.5348
	0.0287	-0.8062	0.5419	0.2376
	0.0405	-0.4717	-0.3463	-0.8109
C(2)	0.0267	-0.9068	0.4187	0.0501
	0.0608	0.0468	-0.0183	0.9987
	0.0516	0.4191	0.9080	-0.0030
C(3)	0.0901	-0.3434	-0.7343	0.5856
	0.0399	0.9231	-0.3787	0.0664
	0.0460	0.1730	0.5633	0.8079
C(4)	0.0966	-0.3369	-0.9259	0.1706
	0.0376	0.5276	-0.0356	0.8487
	0.0545	-0.7798	0.3760	0.5005
C(5)	0.0749	0.5506	0.8245	0.1306
	0.0442	0.1889	-0.2754	0.9426
	0.0563	0.8131	-0.4944	-0.3074
C(6)	0.0606	0.2901	0.8341	0.4691
	0.0436	-0.3254	-0.3750	0.8681
	0.0487	0.9000	-0.4045	0.1626
C(7)	0.0601	-0.4443	-0.8729	0.2016
	0.0357	0.0374	0.2068	0.9777
	0.0403	-0.8951	0.4419	-0.0592
C(8)	0.0651	-0.4046	-0.8301	0.3836
	0.0387	0.8836	-0.2468	0.3979
	0.0470	-0.2356	0.5000	0.8334
C(9)	0.0353	0.4776	0.6604	0.5795
	0.0917	-0.8528	0.5071	0.1249
	0.0861	-0.2114	-0.5539	0.8053

TABLE 1.9

INTERATOMIC DISTANCES (< 4 Å)

Intramolecular distances

Atom A	Atom B	A-B	Atom A	Atom B	A-B
C(1)	O	2.398	C(3)	Cl	2.669
C(1)	C(5)	2.419	C(3)	C(6)	2.741
C(1)	C(3)	2.419	C(3)	C(7)	3.799
C(1)	C(8)	2.506	C(4)	C(6)	2.387
C(1)	Cl	2.756	C(5)	C(7)	3.744
C(1)	C(4)	2.790	C(6)	C(7)	2.463
C(1)	C(9)	3.589	C(6)	C(8)	2.828
C(2)	C(6)	2.384	C(6)	C(9)	3.583
C(2)	C(4)	2.386	C(6)	O	3.609
C(2)	C(7)	2.533	C(7)	C(9)	2.641
C(2)	C(5)	2.763	C(7)	Cl	3.178
C(2)	O	2.962	C(8)	O	2.280
C(2)	C(8)	3.810	C(9)	O	3.367
C(3)	C(5)	2.373	O	Cl	2.886

Intermolecular distances

Atom A	Atom B	E.P.*	Cell**	A-B
C(1)	C(2)	1	1 0 0	3.567
C(1)	Cl	1	1 0 0	3.731
C(1)	C(3)	1	1 0 0	3.809

P . T . O .

TABLE 1.9 Cont.

Atom A	Atom B	E.P.*	Cell**			A-B
C(2)	Cl	1	1	0	0	3.780
C(3)	Cl	3	0	0	0	3.670
C(4)	C(3)	1	1	0	0	3.819
C(5)	C(4)	1	1	0	0	3.532
C(5)	C(3)	1	1	0	0	3.634
C(5)	C(6)	3	0	1	0	3.691
C(6)	C(3)	1	1	0	0	3.640
C(6)	C(2)	1	1	0	0	3.679
C(6)	C(6)	3	0	1	0	3.754
C(6)	C(4)	1	1	0	0	3.793
C(6)	C(1)	1	1	0	0	3.841
C(7)	Cl	1	1	0	0	3.706
C(7)	C(2)	1	1	0	0	3.810
C(8)	C(7)	1	1	0	0	3.714
C(9)	O	4	1	1	1	3.212
C(9)	Cl	4	0	1	1	3.543
C(9)	C(8)	1	1	0	0	3.651
C(9)	Cl	4	1	1	1	3.720
C(9)	C(7)	1	1	0	0	3.852
O	C(4)	2	0	0	0	3.421

P . T . O .

TABLE 1.9 Cont.

Atom A	Atom B	E.P.*	Cell**	A-B
O	C(4)	2	1 0 0	3.559
O	Cl	1	1 0 0	3.635
O	C(5)	2	0 0 0	3.704

* Integers under this column refer to the equivalent positions

1) x , y , z ;

2) x , 1/2 - y , 1/2 + z ;

3) -x , -y , -z ;

4) -x , -1/2 + y , -1/2 - z .

** For any distance the triple set of integers given under this column indicate the unit-cell translation that must be added to the appropriate equivalent position to derive the co-ordinates of the atom under the column Atom B from those given in Table 1.4 .

TABLE 1.10

Deviations (Å) of the atoms from the mean planes through

a) all atoms

b) benzene ring atoms C(1) to C(6)

c) C(1) , C(7) , C(8) , C(9) and □ .

	(a)	(b)	(c)
Cl.....	-0.106	-0.030	-
□	0.161	0.160	0.001
C(1)	0.013	-0.005	0.001
C(2)	-0.015	0.012	-
C(3)	-0.044	-0.008	-
C(4)	-0.005	-0.004	-
C(5)	0.057	0.012	-
C(6)	0.046	-0.008	-
C(7)	0.062	0.033	0.010
C(8)	-0.066	-0.143	-0.025
C(9)	-0.103	-0.220	0.014

2.1.8 Discussion

In o-chlorobenzolacetylene the Cl...O and Cl...C(7) intramolecular separations are 2.886 ± 0.005 and 3.178 ± 0.006 Å respectively, which are shorter than the sums of the normal van der Waals' radii (3.20 and 3.80 Å respectively). The corresponding distances in o-chlorobenzoic acid (Ferguson and Sim, 1961) are 2.892 and 3.217 Å respecively. The molecule is therefore expected to be subject to some strain.

The best plane through all the atoms in the molecule, calculated by the method of Schomaker et al., has the equation

$$0.8694\,X' - 0.4062Y - 0.2813Z' + 1.3455 = 0 \qquad (11)$$

where X', Y and Z' (in Å) are referred to the orthogonal axes parallel to a^*, b and c. The root mean square (r.m.s.) distance of the atoms from this mean plane is 0.08 Å. The appropriate χ^2 test (See Sec. I, 1.8.5) shows the significant non-planarity of the molecule. The displacements of different atoms from this mean plane can be seen in Table 1.10(a); the deviations of Cl, C(9) and O appear to be significant.

The equation of the mean plane through the carbon atoms of the benzene ring is

$$0.8542X' - 0.4371Y - 0.2817Z' + 1.4401 = 0 \qquad (12)$$

The r.m.s. distance (0.009 Å) of the atoms C(1) to C(6) and the insignificant deviations of the individual aromatic atoms[Table 1.10(b)] indicate the planarity of the benzene ring. The appropriate χ^2 tests also support this view.

From the Table 1.10 (b) and Fig. 1.6 it is evident that C(2) - Cl and C(1) - C(7) bonds are bent in opposite directions out of the aromatic plane by about 1.4° in each case. This bending, although small, might be significant in relieving overcrowding in the regions of Cl...C(7) and Cl...O.

The mean plane of best fit through C(1), C(7), C(8), C(9) and O atoms, has the equation

$$0.8881X' - 0.3261Y - 0.3240Z' + 1.1033 = 0 \qquad (13)$$

The r.m.s. distance of these atoms from the mean plane is 0.013 Å.

Deviations of the atoms from this mean plane are given in Table 1.10(c). The dihedral angle between this plane and the aromatic plane (12) is 7.1°. The corresponding angle in o-chlorobenzoic acid (Ferguson and Sim, 1961) is 13.7°. This decrease might be due to the intermolecular hydrogen bonding from the acetylenic carbon, C(9), and the carbonyl oxygen of the neighbouring molecule. The rotation of the ethynyl carbonyl group about the C(1) - C(7) bond has significantly relieved the strain of intramolecular overcrowding. Further relief is afforded by significant inplane splaying out of the C(1) - C(7) and C(2) - Cl bonds away from one another (See Fig. 1.6). The strain of overcrowding in the molecule is, therefore, relieved mainly in three different ways.

(i) The ethynyl-carbonyl group is rotated about C(1) - C(7) bond through 7.1° to increase the distance from Cl to O.

(ii) The chlorine and the exocyclic carbon, C(7), are displaced out of the aromatic plane in opposite directions so as to increase the intramolecular distances from the Cl atom to the other affected atoms.

(iii) Distortion of the valency angles C(1) - $\widehat{C(2)}$ -Cl and C(1) - $\widehat{C(7)}$ - O has increased the intramolecular separations between Cl to C(7) and Cl to oxygen.

The carbon-chlorine bond length of 1.734 $\pm$ 0.006 Å is similar to 1.737 Å obtained in o-chlorobenzoic acid (Ferguson and Sim, 1961) and 1.739 Å in 2-chloro-1, 8-phthaloylnaphthalene (See Chapter IV).

The average of the C-C bond lengths in the benzene ring is 1.383 $\pm$ 0.009 Å. Since the molecular librations were not applied to the atomic co-ordinates, it is quite probable that for some of the atoms of the benzene ring, the true atomic centres are not at the apparent centres of electron density, with a consequent decrease in the observed bond lengths. Thus in one bond, C(3) - C(4), which appears surprisingly short (1.346 Å), the thermal parameters indicate a high degree of anisotropy.

The exocyclic C(1) - C(7) bond length (1.474 $\pm$ 0.009 Å) is quite in agreement with 1.479 Å estimated by Dewar and Schmeising (1959) for single bond distance between carbon atoms in the sp^2 - state of hybridisation. In butadiene, (Marais, Sheppard and

Stoicheff, 1962) the length of the identical bond is 1.476 $\pm$ 0.01 Å. The carbon-oxygen double bond (1.227 $\pm$ 0.007 Å) is near to the accepted value of 1.23 $\pm$ 0.01 Å (Int. Tables, Vol. III, 1962). The bond length, C(7) - C(8), is 1.447 $\pm$ 0.009 Å and is about the expected value for a single bond between sp and sp^2 - hybridised carbon atoms. The triple bond, C(8) - C(9), (1.195 $\pm$ 0.09 Å) does not differ significantly from the agreed value of 1.206 $\pm$ 0.005 Å (Tables of Interatomic Distances 1958, 1965). The atoms C(7), C(8) and C(9) are not colinear. The angle C(7) - $\widehat{C(8)}$ - C(9) is 176.6°. Electron factors and the intermolecular packing force involved in the ethynyl hydrogen bonding might be responsible for this bending.

The shortest intermolecular contact (3.212 $\pm$ 0.007 Å) occurs with the ethynyl hydrogen bond. The locations of the hydrogen atoms were not determined accurately. If the ethynyl carbon hydrogen distance (1.06 Å) and angle C - $\widehat{C}$-H (180°) are assumed (Tables of Interatomic Distances 1958, 1965) then the intermolecular H...O separation becomes only 2.2 Å, much less than the corresponding van der Waals contact distance of 2.4

to 2.6 Å. Details of the distances and angles associated with the atoms involved in the intermolecular ethynyl hydrogen bonding can be seen in Fig. 1.7. Further discussion of the ≡ CH...O bonding is carried out in Chapter 5 of this section. All other intermolecular contacts (Table 1.9) correspond to normal van der Waals interactions.

CHAPTER 2

o-BROMOBENZOYLACETYLENE

2.2 INTRODUCTION

o-Bromobenzoylacetylene is not isomorphous with o-chlorobenzoylacetylene. Unlike the latter, it crystallises in the orthorhombic system.

In the infra-red absorption spectrum of o-bromobenzoylacetylene, a maximum corresponding to the ethynyl hydrogen stretching frequency occurs in cyclohexane solution at 3304 $cm.^{-1}$, and at 3222 $cm.^{-1}$ in the solid state. This has been attributed to intermolecular hydrogen bonding between the ethynyl ≡ CH groups and the carbonyl oxygen atoms (Tyrrell, 1963). In view of the presence of the relatively acidic ethynyl hydrogen and the basic carbonyl oxygen, such intermolecular hydrogen bonding is also ususally expected.

A preliminary analysis of the structure, with limited data, has already been done by Ferguson and Tyrrell (1965). The object of the present work was to complete the refinement using more three dimensional data.

2.2.1 Crystal data

o-Bromobenzoylacetylene, C_9H_5OBr, M = 208.9, m.p. = 46°C, orthorhombic, a = 3.94 ± 0.02, b = 7.30 ± 0.03, c = 27.43 ± 0.05 Å, U = 789 Å^3, Dm = 1.74 gm./cc. (by flotation), Z = 4, Dc = 1.76 gm./cc., F(000) = 408, space group $P2_12_12_1$ (D_2^4, No. 19, Int. Tables, Vol. I, 1965); absorption coefficient for x-rays of wave length 1.542 Å, μ = 54.4 cm.$^{-1}$.

2.2.2 Intensity data

Out of the 721 observed planes, used for refinement, 160 were 3 kℓ spectra, estimated visually from equi-inclination Weissenberg photograph; 561 planes were of the 0kℓ-2kℓ reciprocal nets, collected and estimated visually by Ferguson in the same way. The intensity data were corrected for appropriate Lorentz, polarisation and rotation factors (See Sec. I, 1.3.3); but the absorption corrections were ignored.

The ratio of the square of the atomic number of the heavy atom to the sum of the squares of the atomic numbers of the rest of

the atoms per asymmetric unit is

$$\gamma = \frac{f_H^2}{\Sigma f_R^2} = 3.12 \qquad (1)$$

This shows the dominating influence of the heavy atom (See Sec. I, 1.6.3).

2.2.3 Least squares refinement of the structure

Starting with Ferguson's atomic parameters, the structure was refined in ten cycles of full matrix least squares. The progress of the refinement of the structure can be seen in Table 2.1.

The initial job in the refinement of the structure was to place the two sets of data on the same absolute scale. The first cycle of full matrix least squares refinement with isotropic temperature factor was done to get suitable individual layer scale factors. In this cycle, the scale factor for each of the layers was initially chosen to be unity and unit weight was applied to all the data. At the end of this cycle, the layer scale factors for $0k\ell$ to $2k\ell$ spectra were found to be near to one, while that of the $3k\ell$ planes was almost

halved. In the next cycle no appreciable change of the individual layer scales was noticed. The data were then rescaled using the refined scale factors and the full matrix least squares refinement of the positional and isotropic thermal parameters and layer scale factors was continued. Henceforth the weighting scheme used was of the type suggested by Cruickshank et al. (1961), i.e.

$$\sqrt{w} = 1/(p_1 + |F| + p_2|F|^2 + p_3|F|^3)^{\frac{1}{2}} \qquad (2)$$

up to the fourth cycle of refinement, the values of the constants used were

$$p_1 = 2|F|_{min.} = 8, \quad p_2 = 2/|F|_{max.} = 0.0133 \text{ and } p_3 = 0.$$

At every stage of major change in the mode of the refinement, the values of these constants were adjusted so as to be sure that the mean $\Sigma w\Delta^2$ for all groups of planes batched in the order of increasing structure amplitudes ($|F|$) and $\sin\theta/\lambda$ was roughly constant.

At the end of three cycles of isotropic least squares refinement, the residual, R, was 0.115 and no appreciable change

in the atomic parameters was noticed. A three dimensional difference synthesis was then computed. In the resultant electron density distribution, peaks were noticed in the probable hydrogen positions, the anisotropic vibrational characteristics of the atoms were also revealed. The absence of any other significant peaks, showed the correctness of the structure.

Before switching over to the refinement of anisotropic thermal parameters, all the structure amplitudes were rescaled again with the refined individual layer scale factors. Thenceforth a single overall scale factor was refined.

Due to the dominating influence of the heavy atom (Br), the hydrogen locations revealed in the difference map, could not be expected to be accurate and hence on the assumption of standard bond lengths and angles, these were calculated and were introduced into the subsequent cycles of least squares refinement but not refined.

After one cycle of full matrix anisotropic least squares refinement, it was found that the average $\Sigma w\Delta^2$ was high for strong

planes, which were subject to extinction. Therefore, the value of p_3 was changed to 0.0003 and the refinement was continued. In the ninth cycle, the weighting scheme (2) was slightly adjusted again ($p_1 = 6$, $p_2 = 0.0133$ and $p_3 = 0.0004$). In the next cycle, the parameter shifts were less than one third of the corresponding estimated standard deviations indicating that the refinement had converged. In the weighting analysis, all the batches of data were seen to possess similar average $\Sigma w\Delta^2$ which is evident from Table 2.2. A three dimensional difference synthesis was then computed using the phases calculated from the positions of the non-hydrogen atoms only. In this map, the hydrogen locations were clearly revealed. The appropriate sections of this synthesis are shown in Fig. 2.1., superimposed on the final three dimensional electron density distribution. No other significant features were noticed in this map. The R factor at this stage is 0.073. The final values of the measured and calculated structure amplitudes are shown in Table 2.3.

In the structure factor calculations, the atomic scattering curves used, were those of Int. Tables, Vol. III (1962).

2.2.4 Final atomic parameters, molecular dimensions etc.

The final three dimensional electron density distribution of the heavier atoms and the hydrogen positions from the last difference synthesis are shown in Fig 2.1 as superimposed contour sections drawn parallel to (100). The arrangement of the molecules, viewed along the short a axis, is presented in Fig. 2.2. Bond lengths and angles are in Fig. 2.3 which also contains the numbering scheme used for identifying the atoms of a molecule. The distances and angles involved in the intermolecular ethynyl hydrogen bond are presented in Fig. 2.4.

The progress of the refinement, the final weighting analysis and the structure factor agreements are shown in Tables 2.1, 2.2 and 2.3 respectively. The fractional co-ordinates and estimated standard deviations of the non-hydrogen atoms are in Table 2.4 and the corresponding orthogonal co-ordinates with reference to the crystallographic axes and estimated standard deviation (in $\mathring{A}$) are in Table 2.5. Table 2.6 contains the calculated fractional co-ordinates of the hydrogen atoms.

Anisotropic thermal vibrations and estimated standard deviations are in Table 2.7. These are the values of U_{ij} which are defined by the eqn. 16 (Sec. I). Some short intramolecular and intermolecular distances are presented in Table 2.8 and the displacements of atoms from various mean planes are shown in Table 2.9.

The average estimated standard deviations of the bond lengths are, carbon-carbon (0.02 Å), carbon-oxygen (0.02 Å) and carbon-bromine (0.013 Å). The average estimated standard deviation of the valency angles is 1.4°.

DIAGRAMS AND TABLES

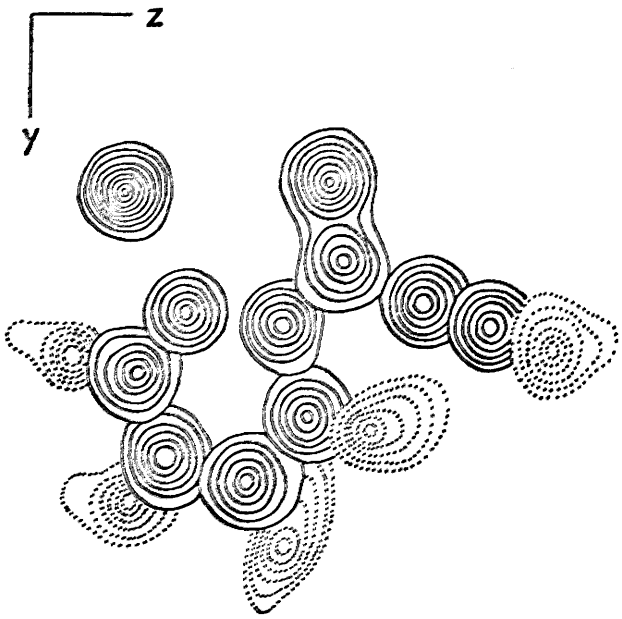


FIG. 2.1

The composite final electron density synthesis (solid contours) for the non-hydrogen atoms, viewed down a-axis and the hydrogen peaks (broken contours) obtained from the difference synthesis computed at the end of the refinement. Contour levels are at 0.1 e/$Å^3$ around the hydrogen atoms starting at the 0.3-electron level. For other atoms contour levels are at 1 e/$Å^3$ except around Br (4 e/$Å^3$) starting at one electron level.

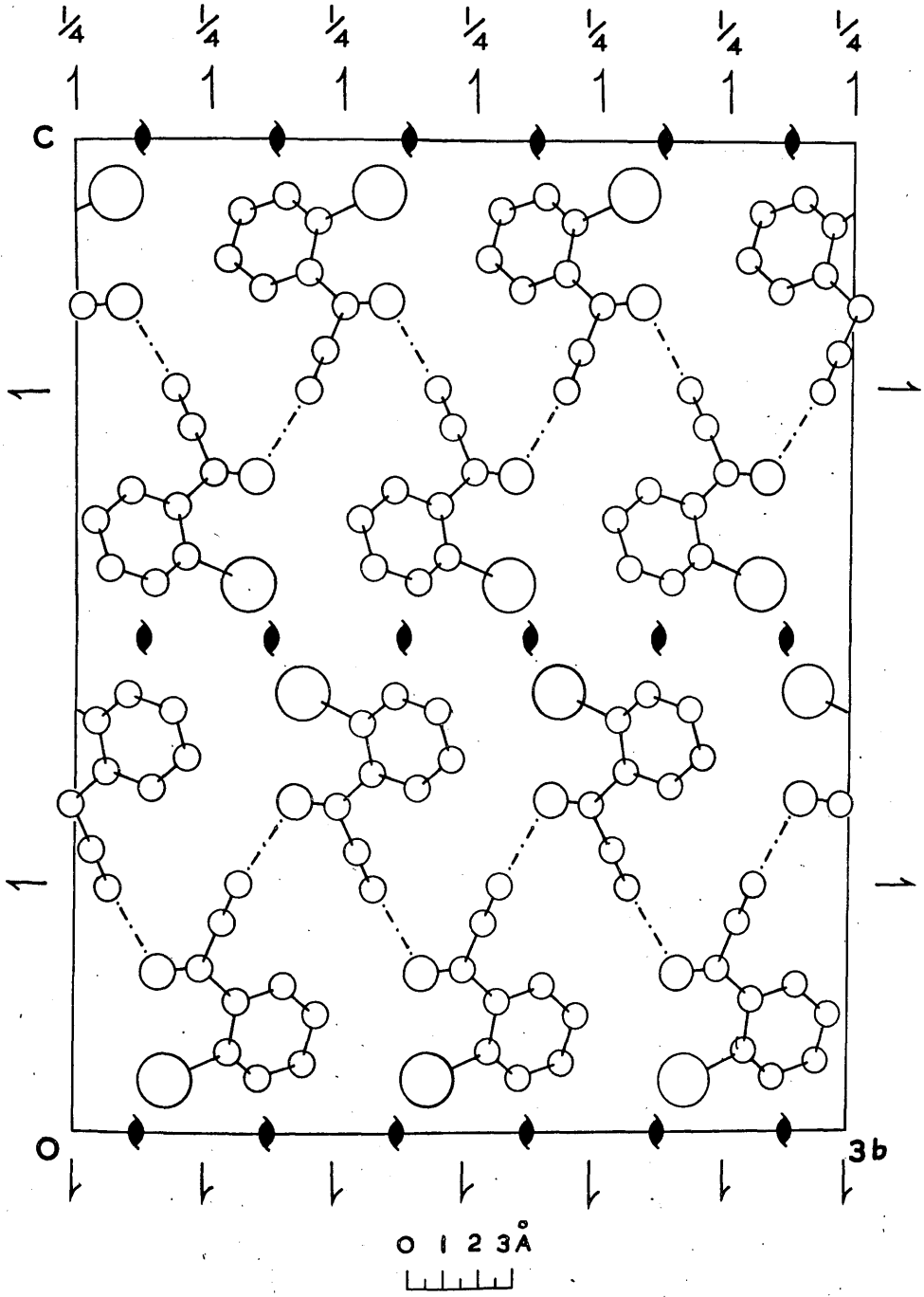


FIG. 2.2

The molecular packing viewed down a-axis.

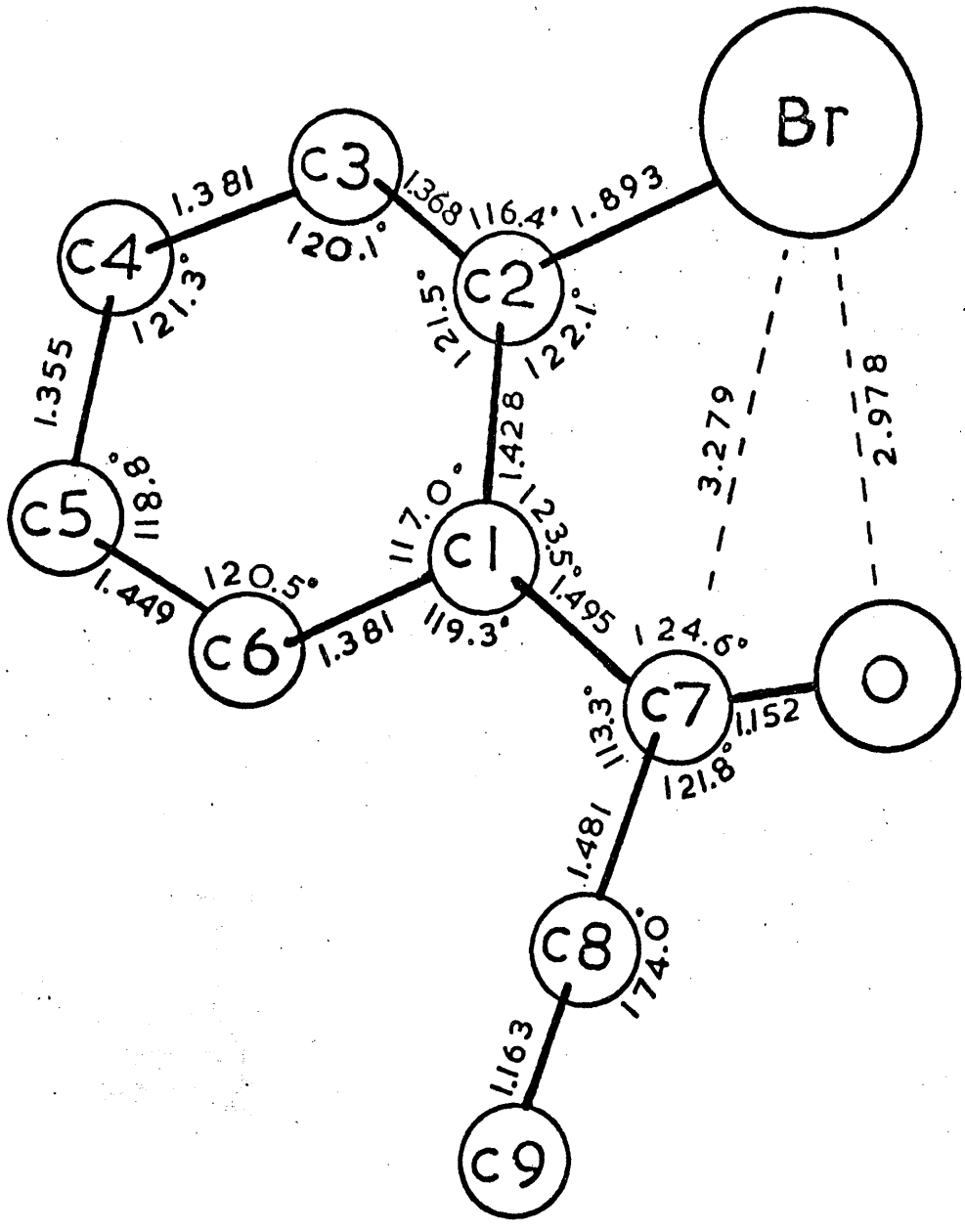


FIG. 2.3

The molecular diagram showing the intramolecular bonded distances (in Å), valency angles (in degrees) and the numbering scheme used for the non-hydrogen atoms (the hydrogen atoms have the same numbers as the carbon atoms to which they are bonded.

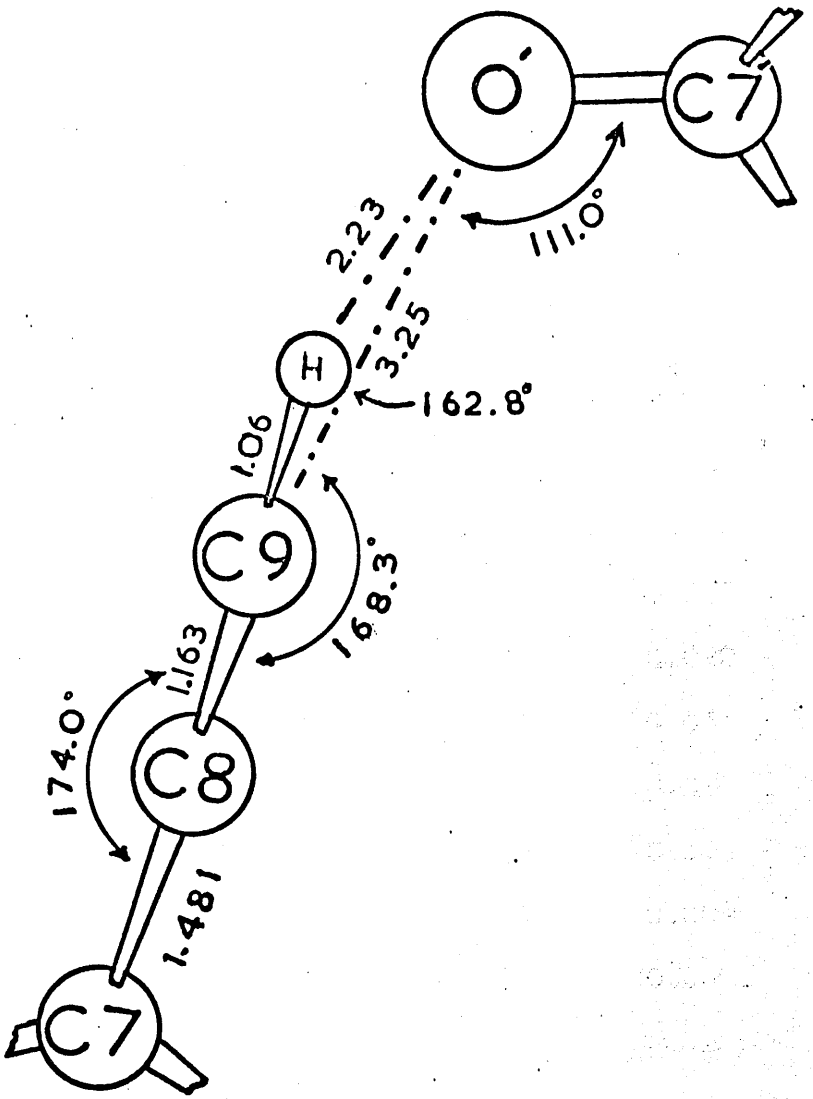


FIG. 2.4

The distances and angles associated with the atoms involved in the intermolecular ≡C-H...O bonding.

TABLE 2.1

PROGRESS OF THE REFINEMENT

Cycle	R factor	$\Sigma w\Delta^2$	$R'=\Sigma w\Delta^2 / \Sigma w \lvert Fo \rvert^2$
[a] 1	0.290	29764	0.078
2	0.140	275	0.037
[b] 3	0.135	258	0.032
4	0.114	201	0.022
[c] 5	0.115	189	0.022
[d] 6	0.078	80	0.011
7	0.075	75	0.010
8	0.073	72	0.009
[e] 9	0.073	71	0.009
10	0.073	71	0.009

a) Refinement of individual layer scales , isotropic thermal and positional parameters using unit weight for all data .

b) Scaled |Fo| and the refinement is continued using a specific weighting scheme .

c) Difference synthesis, scaled |Fo|, hydrogen locations introduced; refinement of overall scale factor, positional and anisotropic thermal parameters.

d) Adjustment of weighting scheme.

e) Further adjustment of weighting scheme.

TABLE 2.2

WEIGHTING ANALYSIS

|F| Obs.	Sin θ /λ				
	0.0-0.4	0.2-0.4	0.4-0.6	0.6-0.8	Totals
0 - 6	0.358/2	0.000/0	0.100/18	0.078/20	0.102/40
6 - 13	0.000/0	0.101/21	0.091/149	0.095/33	0.093/203
13 - 25	0.007/3	0.083/79	0.103/200	0.200/5	0.098/287
25 - 51	0.089/16	0.126/84	0.094/41	0.000/0	0.112/141
51 - 102	0.078/15	0.086/32	0.000/0	0.000/0	0.084/47
102 - up	0.041/3	0.000/0	0.000/0	0.000/0	0.041/3
Totals	0.089/39	0.102/216	0.098/408	0.099/58	0.098/721

Figures on the two sides of the strokes indicate

(Average $\Sigma w\Delta^2$ in the group)/(Total planes in the batch).

TABLE 2.3

MEASURED AND CALCULATED STRUCTURE AMPLITUDES

H	K	L	|Fo|	|Fc|
0	0	4	37.1	39.6
0	0	6	143.1	141.1
0	0	8	146.2	146.5
0	0	10	22.2	22.5
0	0	12	25.7	24.9
0	0	14	28.7	27.4
0	0	16	70.6	68.4
0	0	18	44.2	45.9
0	0	20	31.4	31.6
0	0	22	2.2	2.8
0	0	24	9.2	6.2
0	0	26	27.1	27.1
0	0	28	46.1	46.2
0	0	30	16.2	16.2
0	0	32	36.9	36.9
0	0	34	9.9	9.4
1	0	1	51.6	51.6
1	0	2	29.5	29.5
1	0	3	36.9	36.9
1	0	4	31.1	31.1
1	0	5	31.1	31.1
1	0	6	27.1	27.1
1	0	7	46.1	46.1
1	0	8	27.1	27.1
1	0	9	36.9	36.9
1	0	10	42.6	42.6
1	0	11	36.9	36.9
1	0	12	36.9	36.9
1	0	13	36.9	36.9
1	0

TABLE 2.4

FRACTIONAL COORDINATES AND E.S.D.S.

Atom	x/a	y/b	z/c
Br	0.0527 ± 5	0.3529 ± 2	0.0551 ± 1
O	0.1814 ± 39	0.3212 ± 16	0.1618 ± 4
C(1)	0.0126 ± 31	0.6135 ± 16	0.1354 ± 4
C(2)	-0.0647 ± 39	0.5769 ± 18	0.0855 ± 4
C(3)	-0.2230 ± 37	0.7041 ± 21	0.0568 ± 4
C(4)	-0.2904 ± 44	0.8769 ± 22	0.0748 ± 5
C(5)	-0.2231 ± 51	0.9209 ± 21	0.1218 ± 6
C(6)	-0.0445 ± 44	0.7895 ± 21	0.1520 ± 4
C(7)	0.1736 ± 44	0.4767 ± 23	0.1687 ± 5
C(8)	0.3000 ± 49	0.5580 ± 24	0.2147 ± 4
C(9)	0.4206 ± 50	0.6097 ± 21	0.2509 ± 5

TABLE 2.5

ORTHOGONALISED COORDINATES AND E.S.D.S. (Å)
REFERRED TO THE CRYSTALLOGRAPHIC AXES

ATOM	X	Y	Z
Br	0.207 ± 2	2.576 ± 2	1.512 ± 1
O	0.715 ± 15	2.344 ± 12	4.437 ± 12
C(1)	0.049 ± 12	4.479 ± 12	3.714 ± 10
C(2)	-0.255 ± 15	4.212 ± 13	2.345 ± 12
C(3)	-0.879 ± 15	5.140 ± 15	1.557 ± 12
C(4)	-1.144 ± 17	6.401 ± 16	2.052 ± 15
C(5)	-0.879 ± 20	6.722 ± 16	3.341 ± 15
C(6)	-0.175 ± 17	5.763 ± 15	4.168 ± 12
C(7)	0.684 ± 17	3.480 ± 17	4.629 ± 15
C(8)	1.182 ± 20	4.073 ± 18	5.890 ± 12
C(9)	1.657 ± 20	4.451 ± 15	6.882 ± 15

TABLE 2.6

ASSUMED FRACTIONAL CO-ORDINATES OF THE HYDROGEN
ATOMS AND ISOTROPIC TEMPERATURE FACTORS

ATOM	x/a	y/b	z/c	Uiso
H(3)	-0.296	0.669	0.020	0.04
H(4)	-0.399	0.979	0.050	0.05
H(5)	-0.309	1.050	0.137	0.05
H(6)	0.041	0.828	0.188	0.04
H(9)	0.530	0.657	0.284	0.05

TABLE 2.7

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.
$o2$
(in A)

ATOM	U11	U22	U33	2U23	2U31	2U12
Br	0.0483 11	0.0603 10	0.0437 7	-0.0223 13	-0.0066 12	0.0069 14
O	0.1192 95	0.0464 86	0.0513 61	-0.0024 97	-0.0855 159	0.0048 156
C(1)	0.0087 71	0.0398 68	0.0347 50	0.0066 86	-0.0073 86	-0.0067 92
C(2)	0.0250 81	0.0416 70	0.0390 58	-0.0088 96	-0.0015 113	-0.0153 118
C(3)	0.0293 87	0.0605 90	0.0277 54	0.0138 119	0.0150 115	-0.0058 117
C(4)	0.0399 99	0.0555 101	0.0483 67	0.0354 143	-0.0114 126	0.0131 146
C(5)	0.0627 116	0.0394 88	0.0505 75	-0.0030 126	-0.0087 156	0.0185 143
C(6)	0.0321 96	0.0596 86	0.0294 53	0.0101 101	-0.0025 118	0.0033 137
C(7)	0.0364 111	0.0505 98	0.0474 76	0.0163 131	-0.0358 136	-0.0353 131
C(8)	0.0593 118	0.0643 104	0.0235 56	0.0153 119	-0.0245 123	-0.0180 168
C(9)	0.0530 124	0.0636 101	0.0479 72	-0.0013 143	-0.0142 169	-0.0196 191

TABLE 2.8

SOME SHORT INTERATOMIC DISTANCES

Intramolecular distances (<3.4Å)

Atom A	Atom B	A - B (Å)	Atom A	Atom B	A - B (Å)
Br	C(3)	2.784	C(2)	C(4)	2.382
Br	C(1)	2.914	C(2)	C(6)	2.395
Br	O	2.978	C(2)	C(7)	2.575
Br	C(7)	3.280	C(2)	C(5)	2.772
O	C(8)	2.306	C(3)	C(5)	2.384
O	C(1)	2.350	C(3)	C(6)	2.775
O	C(2)	2.967	C(4)	C(6)	2.414
O	C(9)	3.362	C(6)	C(7)	2.482
C(1)	C(3)	2.439	C(6)	C(8)	2.768
C(1)	C(5)	2.457	C(7)	C(9)	2.640
C(1)	C(8)	2.486	C(1)	C(4)	2.808

Intermolecular distances (<3.8Å)

Atom A	Atom B	E.P.*	Cell**	A - B(Å)
Br	C(4)	1	0 -1 0	3.767
O	C(9)	2	1 -1 0	3.253
O	C(5)	1	0 -1 0	3.504
O	C(9)	2	0 -1 0	3.708

P . T . O .

TABLE 2.8 Cont.

Atom A	Atom B	E.P.*	Cell**			A - B (Å)
C(1)	C(7)	1	-1	0	0	3.572
C(1)	C(8)	1	-1	0	0	3.575
C(1)	C(4)	1	1	0	0	3.742
C(1)	C(3)	1	1	0	0	3.763
C(1)	C(5)	1	1	0	0	3.774
C(2)	C(3)	1	1	0	0	3.533
C(2)	C(4)	1	1	0	0	3.767
C(4)	C(6)	1	-1	0	0	3.703
C(5)	C(6)	1	-1	0	0	3.475
C(6)	C(8)	1	-1	0	0	3.534
C(6)	C(9)	1	-1	0	0	3.678
C(7)	C(8)	1	-1	0	0	3.714
C(8)	C(9)	2	1	-1	0	3.579
C(8)	C(9)	1	-1	0	0	3.623
C(9)	C(9)	2	1	0	0	3.704

* Integers refer to the following equivalent positions
(1) x , y , z ;
(2) -x, 1/2 +y , 1/2 - z .

** For any distance the triple set of integers given under this column indicate the unit-cell translation that must be added to the appropriate equivalent position to derive the co-ordinates of the atom under the column Atom B from those given in Table 2.4 .

TABLE 2.9

Displacements (in Å) of atoms from the mean planes through

(a) all atoms ;

(b) aromatic carbon atoms, C(1) to C(6) ;

(c) C(1) , C(7) , C(8) and O .

Atom	(a)	(b)	(c)
Br	0.262	0.154	0.873
O	-0.360	-0.344	-0.008
C(1)	-0.071	-0.035	-0.005
C(2)	0.050	0.017	0.300
C(3)	0.041	-0.007	0.216
C(4)	0.009	0.014	-0.079
C(5)	-0.103	-0.031	-0.377
C(6)	-0.045	0.042	-0.243
C(7)	-0.116	-0.062	0.024
C(8)	0.070	0.198	-0.020
C(9)	0.264	0.448	0.008

2.2.5 Discussion

In o-bromobenzoylacetylene, the intramolecular distances of Br...O (2.978 ± 0.012) and Br...C(7) (3.279 ± 0.013 Å) are both considerably shorter than the appropriate sums of the normal van der Waals' radii (3.35 and 3.95 Å respectively). The corresponding distances in o-bromobenzoic acid are, 3.00 and 3.275 Å respectively. This shows that like o-bromobenzoic acid, the molecules of o-bromobenzoylacetylene are under strain from intramolecular overcrowding.

The equation of the mean plane through all the non-hydrogen atoms of the molecule, calculated by the method of Schomaker et al. (1959) is

$$0.8909X + 0.2970Y - 0.3438Z - 0.1678 = 0 \qquad (3)$$

where X, Y and Z (in Å) are the orthogonal co-ordinates referred to the crystallographic axes. The root mean square distance of the atoms from this plane is 0.16 Å. The corresponding χ^2 test (See Sec. I, 1.8.5) shows that the molecule is significantly non-planar. The distances of the atoms from the mean plane are shown in Table 2.9(a). Br and C(9) are displaced in the same

direction to the same extent whereas the displacement of the carbonyl oxygen in the opposite direction is prominent.

The mean plane through the atoms of the benzene ring has the equation

$$0.8975X + 0.3229Y - 0.3003Z - 0.4100 = 0 \qquad (4)$$

The root mean square distance of the atoms, C(1) to C(6), from this plane is 0.027 Å. The appropriate χ^2 test shows that, within experimental error, the benzene ring is planar. The displacements of atoms from the plane are in Table 2.9(b). Br and the exocyclic carbon, C(7), are displaced out of this plane in opposite directions by 0.154 and -0.062 Å respectively. This corresponds to the angular displacement of valency bonds C(2) - Br and C(1) - C(7) out of the plane by 4.6 and -2.4° respectively. This displacement must help to relieve the strain of intramolecular overcrowding.

The equation of the best plane through the oxygen and C(1), C(7), C(8), C(9) atoms is

$$0.8866X + 0.1270Y - 0.4447Z + 1.0342 = 0 \qquad (5)$$

Displacements of various atoms from this plane [Table 1.9(c)] and the appropriate χ^2 test show that all these five atoms are coplanar. The dihedral angle between this plane and the mean plane through the atoms of the benzene ring is 13.6° compared with 7.1° in the case of o-chlorobenzoylacetylene (described in the last chapter). This shows that the extent of rotation of the ethynyl carbonyl plane around the exocyclic C(1) - C(7) bond has increased with the increase in size of the halogen substituent. Had there been no such rotation, the intramolecular separations of Br...C(7) and Br...O would have been unacceptably short. Further relief of strain of the intramolecular overcrowding is secured through the in-plane splaying out of C(2) - Br, C(1) - C(7) and C(7) - O bonds causing the distortion of valency angles C(1) - $\widehat{C(2)}$ - Br, C(2) - $\widehat{C(1)}$ - C(7) and C(1) - $\widehat{C(7)}$ - O.

In the molecule of o-bromobenzoylacetylene, the carbon-bromine bond length is 1.893 ± 0.013 Å. The corresponding value in o-bromobenzoic acid (Ferguson and Sim, 1962 a) is 1.885 ± 0.014 Å. These values appear to be slightly higher than the standard C - Br distance of 1.85 ± 0.01 Å quoted in Int. Tables, Vol.

III (1962), but similar values have been found in related compounds. In the structure of 4-bromo-3-nitrobenzoic acid, Gemmel (1966) obtained a C-Br distance of 1.91 Å. Cammerman et al. (1965) got an average carbon-bromine bond length of 1.92 Å in 2-o-(p-bromobenzenesulphonyl)-1, 4:3, 6-dianhydro-D-glucitol-5-nitrate.

The average carbon-carbon bond length in the benzene ring, 1.394 Å, is in agreement with the mean standard value of 1.395 ± 0.003 Å (Int. Tables, Vol. III, 1962). The exocyclic C(1) - C(7) bond length, 1.495 Å, is similar to 1.487 Å in o-bromobenzoic acid (Ferguson and Sim, 1962 a). In benzoic acid (Sim, Robertson and Goodwin, 1955) the corresponding bond length is 1.48 Å.

The carbon-oxygen double bond 1.152 ± 0.02 Å is not significantly different from 1.20 ± 0.02 Å in o-bromobenzoic acid. The bond linking the carbonyl carbon to the ethynyl carbon [C(7) - C(8)], 1.481 ± 0.02 Å, is similar to that of 1.45 ± 0.02 Å in vinyl acetylene (Tables of Interatomic Distances). The carbon-carbon triple bond, C(8) - C(9), 1.163 Å, is near to 1.18 Å found for a similar bond in propargyl 2-bromo-3-nitrobenzoate (Calabrese, McPhail and Sim, 1967). The corresponding value in o-chloro-

benzoylacetylene (described earlier) is 1.195 Å. The atoms C(7), C(8) and C(9) are not co-linear; the bond angle C(7) - $\widehat{C(8)}$ - C(9) is 174°. In o-chlorobenzoylacetylene, a similar bending (176.6°) is also noticed.

The shortest intermolecular distance is between the ethynyl carbon atom, C(9), and the carbonyl oxygen atom (3.25 ± 0.02 Å). Due to the dominating influence of the heavy atom, determination of accurate co-ordinates for hydrogen atom (by x-ray diffraction method) is not possible. Therefore, assuming the ethynyl carbon hydrogen distance of 1.06 Å (Tables of Interatomic Distances) and C $-\widehat{C}-$H angle 180°, the -H...O separation was calculated to be 2.22 Å which is less than the sum of the corresponding normal van der Waals' radii (2.6 Å), (Pauling, 1960) and hence the prediction of intermolecular ethynyl hydrogen bonds in the structure of o-bromobenzoylacetylene, based on i.r. studies (Tyrrell, 1963) was confirmed. Distances and angles associated with atoms involved in the hydrogen bond are shown in Fig. 2.4.

No other intermolecular separation is less than the normal van der Waals contact distance (Table 2.8).

CHAPTER 3

o-FLUOROBENZOIC ACID

2.3 INTRODUCTION

The structure of o-fluorobenzoic acid was solved and refined by Krausse and Dunken (1966). While preparing a paper on the correlation of x-ray crystal structure analysis and infra-red absorption spectra for o-halogeno-aroyl compounds (Eglinton, Ferguson, Islam and Glasby, 1967), the tilt of aromatic plane with carbonyl group plane in o-fluorobenzoic acid (21°), was found to be inconsistent with those of o-chlorobenzoic acid, 13.7° (Ferguson and Sim, 1961) and o-bromobenzoic acid, 18.3°, (Ferguson and Sim, 1962 a). On further scrutiny it was found that Krausse and Dunken's co-ordinates for the atoms do not refer to the same molecule but an appropriate transformation, and recalculation of the mean planes by the method of Schomaker et al. (1959), the dihedral angle between these two mean planes was found to be 6.7° (Ferguson and Islam, 1966 b).

In view of the fact that Krausse and Dunken had only 365 independent data at their disposal for the analysis of the structure and inadequate facilities for refinement, their estimated standard

deviations are optimistic.

These factors prompted a new data collection and refinement of structures.

2.3.1 Crystal data

o-Fluorobenzoic acid crystallised from a mixture of acetone and petroleum into beautiful transparent lath shaped crystals elongated along the b axis.

While an attempt was being made to set a crystal on the linear diffractometer, it became obvious that there was an error in Krausse and Dunken's cell dimensions, especially in a, c and β. In order to measure these cell constants accurately, a long exposure equatorial Weissenberg photograph was taken with the crystal rotating about the needle axis b. The crystal was then replaced by a fine Al wire and under identical conditions it was exposed to the x-ray beam for a period of 36 hours in order to record all the high order Al powder lines on the same film. The resulting photograph was then examined and 12 high order diffraction spots ($0.755 < \sin\theta < 0.935$), on or near either side of the high order Al powder lines were indexed. The distances of these spots from the nearest Al lines were measured and from a knowledge of the standard $\sin\theta$ values of the Al lines, corresponding values for all these twelve planes were calculated and hence the cell constants (a, c, and β) were computed.

o-Fluorobenzoic acid, $C_7H_5O_2F$, m.p. = 126°C., M = 140, a = 6.553 ± 0.002, b = 3.813 ± 0.005, c = 24.754 ± 0.007 Å, β = 100.71 ± 0.03°, D_m = 1.51 gm./cc.,(by flotation), Z = 4, D_c = 1.53 gm./cc., F(000) = 288, U = 608 $Å^3$, monoclinic crystals, space group $P2_1/c$ [C_{2h}^5, No.14, (Int. Tables Vol. I, 1965)]; absorption coefficient for Cu Kα (λ = 1.542 Å), μ = 12 $cm.^{-1}$.

2.3.2 Intensity data

Intensity data were collected on equi-inclination Weissenberg photographs of the 0kℓ to 3kℓ reciprocal lattice nets, using the multiple film technique (Robertson, 1943). The crystal was rotated about the needle axis b and was exposed to Ni-filtered Cu Kα radiation (λ = 1.542 Å). Due to the inherent subliming nature of the crystal, a fresh one was used for each layer and the exposure time for each layer was limited to 3 days.

The original idea of collecting the data on the linear diffractometer had to be abandoned because the crystal would have disappeared in a matter of a few days while data were being collected from it.

The visual estimation of 821 independent reflections was carried out by comparing them with a standard calibrated step wedge. An additional 165 unobserved reflections, each assigned a value of half the minimum intensity locally observable, were used in all stages of calculations. The 986 independent intensities were then corrected for the appropriate Lorentz, polarisation and rotation factors (See Sec. I, 1.3.3). The absorption corrections were ignored.

2.3.3 Structure refinement by the least squares methods

Since the intensity data were collected with four different crystals, the first job in the structure refinement was to scale each of the four layers of data on to an appropriate absolute scale. Hence, structure factors were calculated with all the 986 planes of h0ℓ to h3ℓ spectra, using Krausse and Dunken's (1966) atomic parameters, and an initial adjustment of the scale was made so that $K \Sigma|F_o| = \Sigma|F_c|$, for each of the layers. A three dimensional electron density distribution was then computed and the improved atomic locations were picked up using the Fourier Search program

(McGregor, 1966). Further refinement was by the least squares methods. Altogether thirteen cycles of least squares refinement were computed using full matrix methods. The progress of the refinement is shown in Table 3.1.

In the first cycle of least squares refinement adjustment of the individual layer scale factors, isotropic temperature factors and positional parameters was done imparting unit weight to all the data. The intensity data were then scaled with these refined scale factors and the refinement was continued. The weighting scheme used, was that of Cruickshank et al.(1961).

$$\sqrt{w} = 1/(p_1 + |F| + p_2|F|^2 + p_3|F|^3)^{\frac{1}{2}} \qquad (1)$$

up to the eighth cycle of refinement, the values of the constants p_1, p_2 and p_3 were chosen to be $2|F|_{min.}$, $2/|F|_{max.}$ and 0 i.e., 0.5, 0.0224 and 0.0 respectively. At the end of the fourth cycle of refinement no appreciable change in the atomic parameters was noticed. A three dimensional difference synthesis was then computed using $(F_o - F_c)$ as Fourier coefficients. In the

resultant map, no significant features were revealed, except for the hydrogen peaks and the anisotropic vibrational characteristics of the atoms. Instead of calculating the hydrogen positions from this map, these were computed from a consideration of the standard values of the bond lengths and the geometry involved and were introduced in all subsequent cycles of refinement but not refined. The isotropic temperature factors, assigned to the hydrogen atoms, were those of the carbon atoms to which these were bonded. The intensity data were then scaled again with the refined individual layer scale factors and thereafter only an overall scale factor, anisotropic thermal vibrations and the positional parameters were adjusted.

In the seventh cycle, the agreement of the observed and calculated structure amplitudes of the individual planes were checked and it was found that a few high order reflections were showing bad agreement. On thorough examination of the Weissenberg photographs, the misindexing of all these three planes was rectified. One further cycle of least squares refinement was carried out.

In a correct choice of weighting scheme a constant average of $\Sigma w\Delta^2$ for groups of reflections with increasing values of

structure amplitudes ($|F_o|$) and $\sin\theta/\lambda$ should be obtained. From such a scrutiny the values of the constants p_1, p_2 and p_3 of the weighting scheme (1) were adjusted to 1.5, 0.0122 and 0.0008 respectively. At the end of the next cycle, the weighting analysis was again checked and it was found that the data were $\sin\theta$ dependent and the weighting scheme (1), so far being used, would not be adequate to tackle such a problem and hence a new weighting scheme (Macdonald, 1966) was used in the subsequent cycles. Finally the constants of the weighting scheme

$$\sqrt{w} = [\{1 - \exp(-p_1(\sin\theta/\lambda)^2\} \;/\; \{1 + p_2|F_o| + p_3|F_o|^2 + p_4|F_o|^3\}]^{\frac{1}{2}} \qquad (2)$$

adjusted were $p_1 = 4$, $p_2 = 0.3$, $p_3 = 0.001$ and $p_4 = 0.0$.

At the end of a further two cycles of least squares refinement, the parameter shifts were less than one third of the corresponding estimated standard deviations indicating the convergence of the refinement. The residual, R, was 0.106. The structure factors, F', were calculated for the non-hydrogen atoms and the three

dimensional electron density distribution was then computed with $(F_o - F_c')$ as Fourier coefficients. In the resulting difference map, hydrogen peaks were clearly revealed and no other significant features were noticed and hence the convergence of the structure refinement was assumed. The relevant sections of the differnece map containing the hydrogen peaks are shown in Fig. 3.1, with the final three dimensional electron density distribution. The agreement of the observed and calculated structure factors can be seen in Table 3.2.

In the structure factor calculations, the atomic scattering curves used, were those of Int. Tables, Vol. III (1962).

2.3.4 Final atomic parameters, molecular dimensions etc.

The arrangement of the molecules, viewed down the short b axis, can be seen in Fig. 3.2 and the centro-symmetric dimer formations (through intermolecular hydrogen bonds) are shown in Fig. 3.3. The bond lengths, bond angles and the numbering scheme are given in Fig. 3.4.

The final fractional co-ordinates and corresponding estimated standard deviations of the non-hydrogen atoms are shown in Table 3.3 and the fractional co-ordinates of the hydrogen atoms, calculated from the last difference synthesis, are in Table 3.4. The co-ordinates of the heavier atoms referred to the orthogonal axes parallel to a^*, b and c are given in Table 3.5, while Table 3.6 contains the anisotropic temperature factors and their estimated standard deviations. The principal values and direction cosines of anisotropic vibration tensors with reference to the orthogonal axes parallel to a^*, b and c are presented in Table 3.7. Some intramolecular and intermolecular short distances are in Table 3.8 and the displacements of atoms from various mean planes are shown in Table 3.9.

The final estimated standard deviations of the average valency bonds between carbon-carbon, carbon-oxygen and carbon-fluorine are 0.006, 0.005 and 0.004 Å respectively. The average estimated standard deviation of the valency angles is 0.4°.

DIAGRAMS AND TABLES

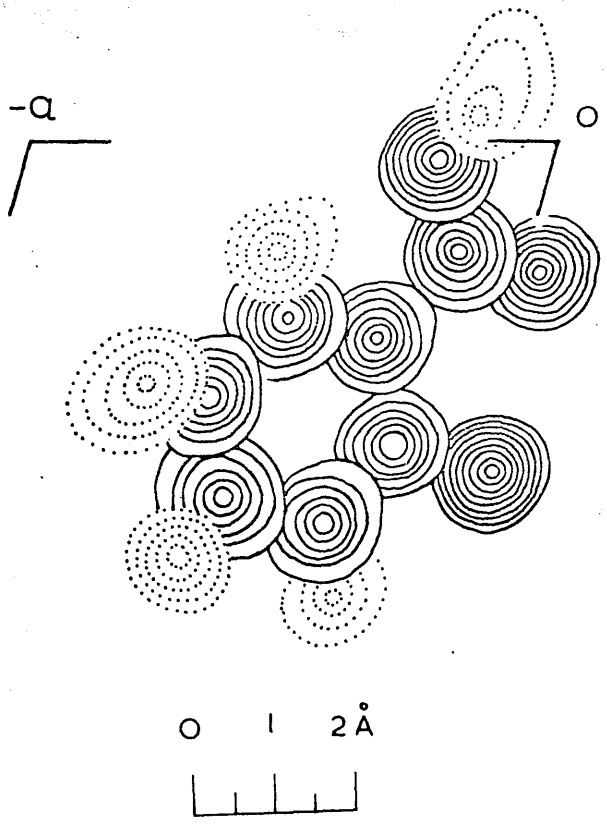


Fig. 3.1

The superimposed sections of the final three dimensional electron density synthesis through the atomic centres of the non-hdrogen atoms (solid contours) parallel to (010). Also shown are the hydrogen peaks (broken contours) obtained from the three dimensional difference synthesis computed at the conclusion of the refinement. Contour intervals are at 0.1 electron per cubic Angstrom around the hydrogen atoms starting at the 0.4 electron level. For other atoms contour intervals are at one electron per cubic Angstrom starting at one electron level.

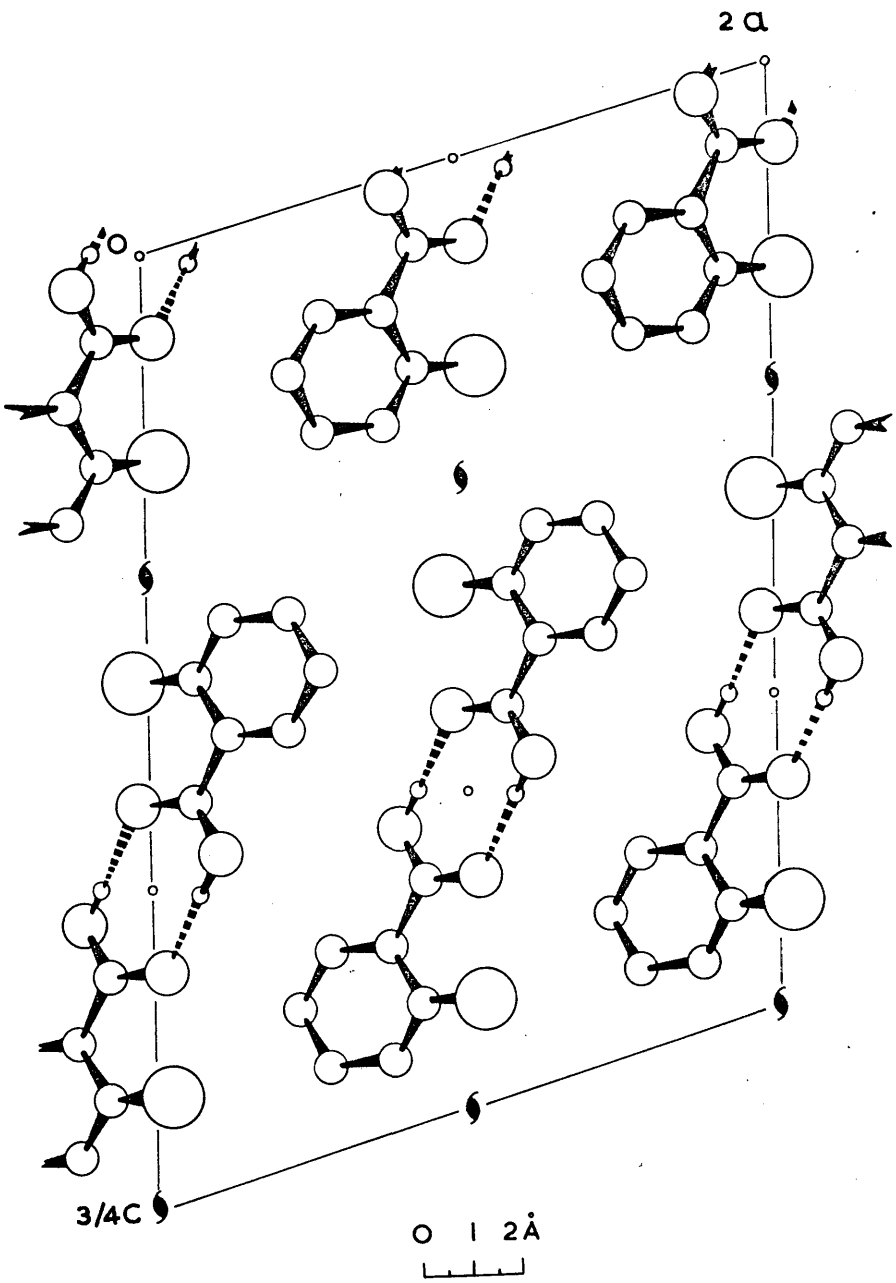


FIG. 3.2

The molecular arrangement viewed down the short b-axis

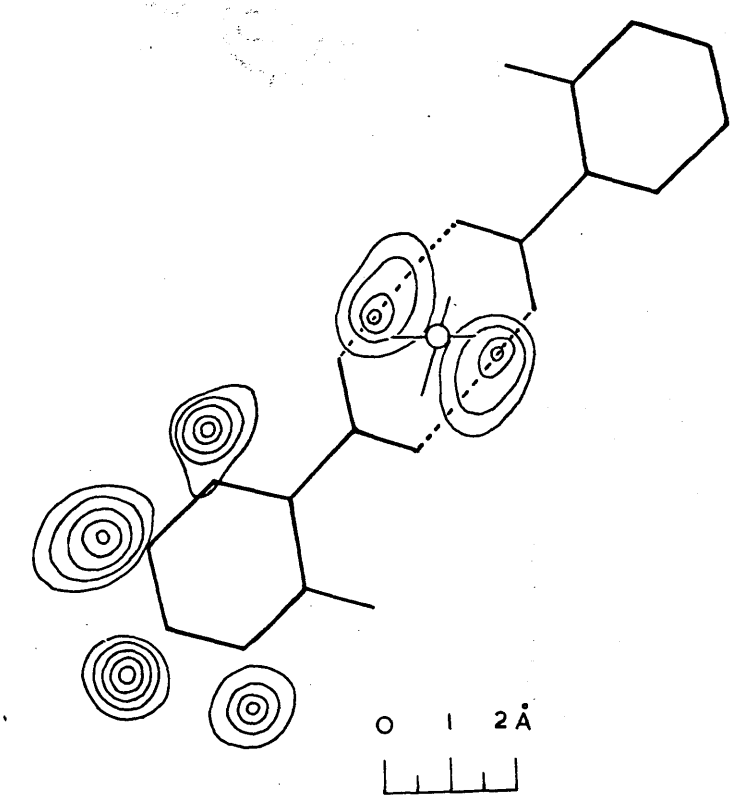


FIG. 3.3

The hydrogen contours from the final three dimensional difference synthesis (contour intervals are at 0.1 e/$\mathring{A}^3$ starting at the 0.4 electron level) and the independent dimer formation through the intermolecular O-H...O bonds.

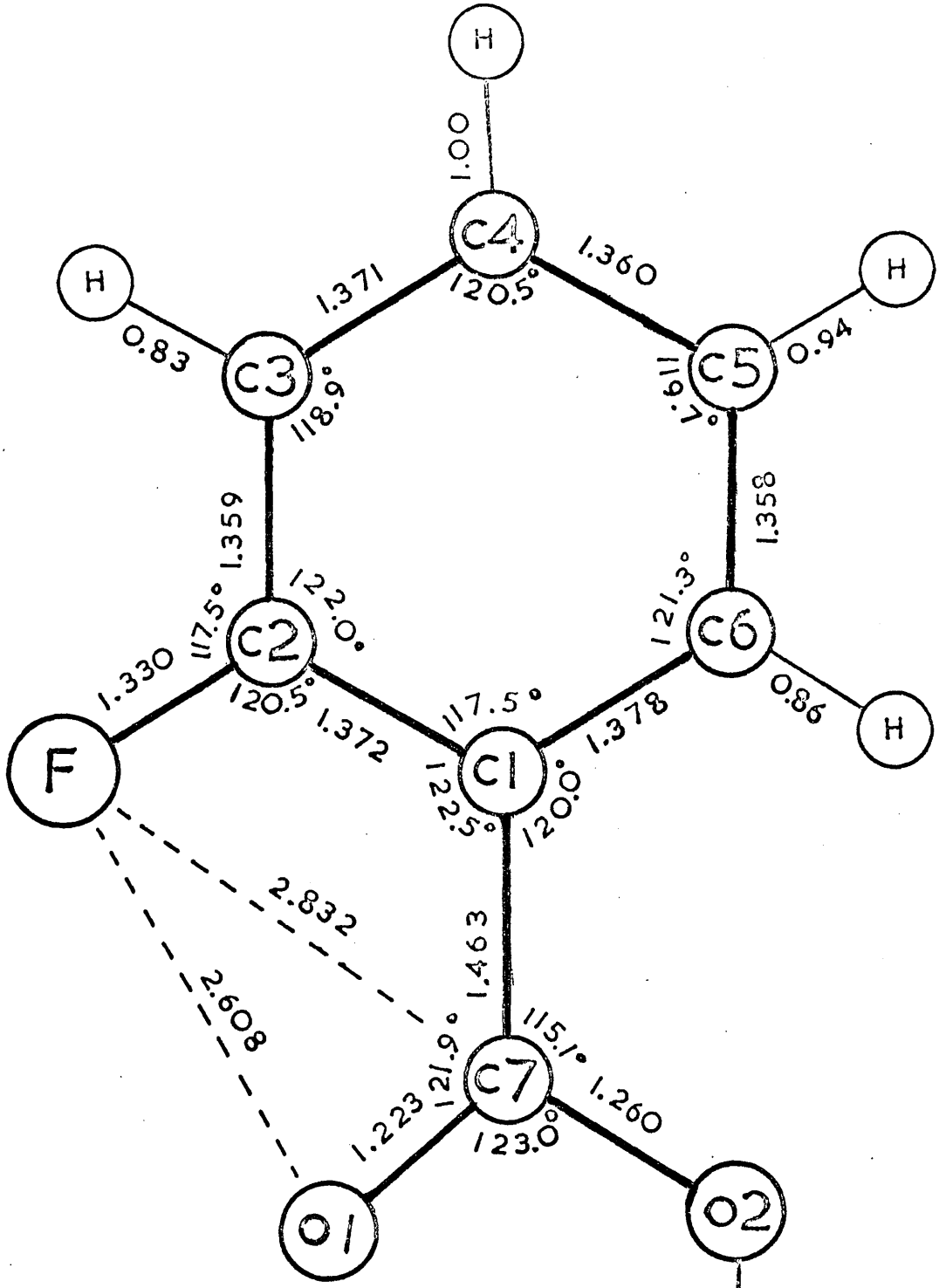


FIG. 3.4

The molecular diagram showing the bond-lengths (in Å) the bond-angles (in degrees) and the numbering scheme used for identifying the non-hydrogen atoms. The hydrogen atoms have the same numbering system as that of the heavier atoms to which they are bonded. The C-H bond-lengths are based on the hydrogen positions obtained from the last difference synthesis.

TABLE 3.1

PROGRESS OF THE REFINEMENT

Cycle	R factor	$w\Delta^2$	$R'=\Sigma w\Delta^2 / \Sigma w\|Fo\|^2$
1[a]	0.234	769.9	0.168
2[b]	0.214	577.3	0.104
3	0.188	373.7	0.076
4[c]	0.188	342.8	0.074
5[d]	0.180	303.4	0.064
6	0.163	232.0	0.057
7[e]	0.161	228.3	0.057
8[f]	0.119	117.8	0.031
9	0.109	96.8	0.026
10[g]	0.107	57.2	0.020
11[h]	0.106	113.3	0.021
12	0.106	110.0	0.021
13	0.106	109.0	0.020

a) Refinement of individual layer scale factors, isotropic thermal vibrations and positional parameters using unit wt. for all data .

b) Scaled intensity data and refinement continued using a specific weighting scheme .

c) Difference synthesis computed and H atoms introduced.

d) Scaled intensity data and refinement of an over all scale factor , positional parameters and anisotropic thermal vibrations started .

e) Indexing error corrected .

f) Values of the constants of weighting scheme adjusted .

g) New weighting scheme used .

h) Weighting scheme further adjusted .

TABLE 3.2

FINAL OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	|Fo|	Fc
7	0	0	4.7	-5.9
7	0	2	2.8	-2.7
7	0	6	2.5	-2.6
7	0	8	2.1	-2.2
6	0	0	4.6	5.0
6	0	2	6.8	-7.4
6	0	4	1.0	0.9
6	0	6	2.9	-3.7
6	0	8	2.3	-2.3
6	0	10	3.4	3.3
6	0	12	3.2	2.9
6	0	14	1.5	1.6
6	0	16	2.4	2.8
5	0	0	6.7	6.8
5	0	2	3.9	-3.4
5	0	4	3.6	4.0
5	0	6	1.0	-0.6
5	0	8	9.2	-10.3
5	0	10	10.9	12.3
5	0	12	13.0	15.6
5	0	14	1.0	1.1
5	0	16	3.0	2.8
5	0	18	3.8	-3.8
5	0	20	3.3	-3.7
4	0	0	23.3	21.0
4	0	2	27.4	-23.3
4	0	4	1.9	1.7
4	0	6	6.8	-7.3
4	0	8	1.0	-1.0
4	0	10	29.2	29.0
4	0	12	3.6	-4.1
4	0	14	10.0	-10.5
4	0	16	5.6	5.2
4	0	18	4.1	-4.1
4	0	20	4.0	-4.0
3	0	22	0.7	0.1
3	0	24	1.8	-1.6
3	0	0	22.5	-22.5
3	0	2	26.1	-24.8
3	0	4	8.2	7.6
3	0	6	9.9	-9.5
3	0	8	19.1	-18.1
3	0	10	5.2	-4.7
3	0	12	6.0	-5.8
3	0	14	2.8	-4.4
3	0	16	1.0	0.9
3	0	18	6.2	-5.7
3	0	20	11.0	-11.6
2	0	0	25.9	29.3
2	0	2	14.4	-13.3
2	0	4	25.8	-23.7
2	0	6	15.8	-14.8
2	0	8	23.2	-21.8
2	0	10	6.6	-5.7
2	0	12	5.0	-4.3
2	0	14	6.4	-6.3
2	0	16	8.5	7.7
2	0	18	2.1	-2.4
2	0	20	7.0	-7.4
2	0	22	8.4	9.6
2	0	24	1.9	1.8
2	0	26	1.3	-1.3
2	0	28	2.7	2.8
1	0	0	27.5	31.7
1	0	2	58.8	69.3
1	0	4	17.9	15.8
1	0	6	36.8	33.7
1	0	8	48.8	41.0
1	0	10	25.6	-24.2
1	0	12	25.7	30.4
1	0	14	13.2	11.6
1	0	16	12.0	12.0
1	0	18	13.6	12.6
1	0	20	2.7	2.9
1	0	22	4.0	4.0
1	0	24	1.0	-0.7
1	0	26	0.9	1.2
1	0	28	3.1	2.6
0	0	2	43.5	-42.9
0	0	4	27.7	29.6
0	0	6	43.5	-42.6
0	0	8	18.7	15.5
0	0	10	33.8	32.1
0	0	12	2.1	1.4
0	0	14	16.0	15.1
0	0	16	12.0	11.2
0	0	18	1.0	0.7
0	0	20	2.7	-2.6
0	0	22	3.8	-3.0
0	0	24	5.6	-5.3
0	0	26	3.3	-2.5
0	0	28	3.5	3.1
0	0	30	30.3	-33.5
0	0	32	14.1	12.5
0	0	34	10.5	-7.9
0	0	36	28.6	-31.7
0	0	38	35.6	-34.3
0	0	40	5.9	6.6
0	0	42	2.1	-1.6
0	0	44	9.2	-3.6
0	0	46	28.4	24.3
0	0	48	11.1	-10.9
0	0	50	27.6	-28.0
0	0	52	2.7	-3.0
0	0	54	6.0	-5.1
0	0	56	0.8	0.1
0	0	58	4.8	4.0
0	0	60	12.6	-14.8
0	0	62	41.1	-47.2
0	0	64	1.0	-0.2
0	0	66	48.3	-55.0
0	0	68	51.7	-55.3
0	0	70	25.9	27.4
0	0	72	3.6	2.8
0	0	74	3.8	3.9
0	0	76	5.6	5.3
0	0	78	27.3	-27.6
0	0	80	3.6	-3.1
0	0	82	5.4	5.2
0	0	84	7.4	-8.5
0	0	86	2.0	1.7
0	0	88	2.5	2.4
0	0	90	18.1	18.0
0	0	92	7.6	-8.0
0	0	94	6.6	-6.2
0	0	96	13.6	-13.2
0	0	98	4.8	4.6
0	0	100	16.2	15.5
0	0	102	2.9	-1.5
0	0	104	6.3	6.8
0	0	106	3.3	3.8
0	0	108	1.7	0.6
0	0	110	2.1	-1.3
0	0	112	1.7	1.5
0	0	114	2.2	1.8
0	0	116	4.0	3.3
0	0	118	2.7	3.2
0	0	120	1.5	1.9
0	0	122	2.6	-2.3
0	0	124	0.7	0.4
1	0	1	1.0	1.0
1	0	3	1.0	0.8
1	0	5	1.0	1.0
1	0	7	1.0	0.9
1	0	9	1.0	0.8
1	0	11	1.0	0.8
1	0	13	1.0	0.8
1	0

TABLE 3.3

FRACTIONAL COORDINATES AND E.S.D.S.

Atom	x/a	y/b	z/c
F	0.0475 ± 4	0.1049 ± 12	0.1718 ± 1
O(1)	0.0339 ± 5	-0.0263 ± 10	0.0678 ± 1
O(2)	-0.2195 ± 6	0.2188 ± 12	0.0107 ± 1
C(1)	-0.2358 ± 6	0.2481 ± 10	0.1026 ± 2
C(2)	-0.1453 ± 6	0.2252 ± 13	0.1571 ± 2
C(3)	-0.2460 ± 8	0.3266 ± 14	0.1978 ± 2
C(4)	-0.4448 ± 8	0.4523 ± 13	0.1839 ± 2
C(5)	-0.5391 ± 7	0.4769 ± 13	0.1302 ± 2
C(6)	-0.4355 ± 6	0.3760 ± 12	0.0902 ± 2
C(7)	-0.1297 ± 6	0.1363 ± 11	0.0585 ± 2

TABLE 3.4

FRACTIONAL CO-ORDINATES OF THE HYDROGEN ATOMS OBTAINED FROM THE LAST DIFFERENCE SYNTHESIS

Atom	x/a	y/b	z/c
H(3)	-0.194	0.369	0.230
H(4)	-0.514	0.537	0.213
H(5)	-0.662	0.611	0.125
H(6)	-0.483	0.386	0.055
H(02)	-0.154	0.414	-0.012

TABLE 3.5

ORTHOGONALISED COORDINATES REFERRED TO THE AXES PARALLEL TO a*,b,c AND E.S.D.S.(in Å)

Atom	X	Y	Z
F	0.306 ± 3	0.400 ± 4	4.196 ± 3
O(1)	0.218 ± 3	-0.100 ± 4	1.638 ± 3
O(2)	-1.413 ± 4	0.834 ± 5	0.532 ± 3
C(1)	-1.518 ± 4	0.946 ± 4	2.827 ± 4
C(2)	-0.936 ± 4	0.858 ± 5	4.066 ± 4
C(3)	-1.584 ± 5	1.245 ± 5	5.196 ± 4
C(4)	-2.864 ± 5	1.724 ± 5	5.093 ± 5
C(5)	-3.471 ± 5	1.818 ± 5	3.880 ± 5
C(6)	-2.804 ± 4	1.434 ± 5	2.762 ± 4
C(7)	-0.835 ± 4	0.520 ± 4	1.606 ± 4

TABLE 3.6

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.
$o2$
(in A)

ATOM	U11	U22	U33	2U23	2U31	2U12
F	0.0636 14	0.1171 29	0.0535 13	0.0207 32	0.0043 22	0.0219 34
O(1)	0.0653 17	0.0652 23	0.0576 15	0.0086 30	0.0202 25	0.0519 33
O(2)	0.0769 20	0.0945 31	0.0500 15	0.0078 34	0.0181 27	0.0610 42
C(1)	0.0557 19	0.0218 21	0.0500 17	0.0068 30	0.0165 29	-0.0105 32
C(2)	0.0570 20	0.0426 26	0.0488 18	0.0094 34	0.0114 30	-0.0017 37
C(3)	0.0808 28	0.0494 30	0.0532 20	-0.0077 39	0.0249 38	-0.0239 48
C(4)	0.0859 30	0.0314 27	0.0736 26	-0.0113 40	0.0666 46	-0.0093 44
C(5)	0.0642 23	0.0350 27	0.0772 26	-0.0014 41	0.0440 40	0.0094 40
C(6)	0.0559 20	0.0340 25	0.0621 21	0.0171 36	0.0177 32	0.0124 37
C(7)	0.0568 19	0.0280 23	0.0469 17	-0.0006 30	0.0086 28	0.0112 34

TABLE 3.7

PRINCIPAL VALUES AND DIRECTION COSINES OF VIBRATION TENSORS REFERRED TO THE AXES PARALLEL TO a*, b and c

ATOM	U / A^2	D1	D2	D3
F	0.1199	0.1721	0.9795	0.1046
	0.0473	0.5969	-0.1882	0.7800
	0.0703	0.7836	-0.0718	-0.6170
O(1)	0.0913	-0.7075	-0.7045	0.0554
	0.0392	0.7067	-0.7052	0.0577
	0.0581	-0.0016	0.0800	0.9968
O(2)	0.1178	-0.6025	-0.7951	0.0696
	0.0488	0.4526	-0.2685	0.8504
	0.0559	-0.6574	0.5438	0.5216
C(1)	0.0204	-0.1379	-0.9812	0.1351
	0.0577	-0.9040	0.1805	0.3876
	0.0500	-0.4047	-0.0687	-0.9119
C(2)	0.0603	-0.8370	0.1846	0.5151
	0.0401	0.0930	-0.8797	0.4663
	0.0497	0.5393	0.4382	0.7192
C(3)	0.0850	-0.9470	0.3154	0.0614
	0.0447	0.3199	0.9068	0.2746
	0.0538	0.0309	0.2797	-0.9596
C(4)	0.0970	0.8544	-0.0985	0.5102
	0.0306	0.0480	0.9926	0.1112
	0.0562	-0.5174	-0.0705	0.8528
C(5)	0.0340	-0.1816	0.9796	0.0862
	0.0803	0.5413	0.0264	0.8404
	0.0587	0.8210	0.1993	-0.5351
C(6)	0.0305	0.2445	-0.9418	0.2309
	0.0648	-0.0061	0.2366	0.9716
	0.0575	-0.9696	-0.2390	0.0521
C(7)	0.0269	-0.1827	0.9831	0.0081
	0.0613	-0.8688	-0.1653	0.4668
	0.0455	0.4603	0.0782	0.8843

TABLE 3.8

INTERATOMIC DISTANCES(<3.5 Å)

Intramolecular distances

Atom A	Atom B	A-B	Atom A	Atom B	A-B
F	C(3)	2.299	C(1)	C(3)	2.388
F	C(1)	2.345	C(1)	C(4)	2.748
F	O(1)	2.608	C(2)	C(6)	2.350
F	C(7)	2.832	C(2)	C(4)	2.350
O(1)	O(2)	2.182	C(2)	C(7)	2.485
O(1)	C(1)	2.351	C(2)	C(5)	2.718
O(1)	C(2)	2.854	C(3)	C(5)	2.371
O(2)	C(6)	2.696	C(3)	C(6)	2.729
O(2)	C(1)	2.301	C(4)	C(6)	2.350
C(1)	C(5)	2.384	C(6)	C(7)	2.459

Intermolecular distances

Atom A	Atom B	E.P.*	Cell**	A - B
F	C(5)	1	1 0 0	3.384
F	C(3)	3	0 0 1	3.416
O(1)	O(2)	2	0 0 0	2.583
O(1)	O(1)	2	0 0 0	3.311

P . T . O .

TABLE 3.8 cont.

Atom A	Atom B	E.P.*	Cell**	A - B
O(1)	C(7)	2	0 0 0	3.329
O(1)	C(7)	1	0 -1 0	3.363
O(1)	C(1)	1	0 -1 0	3.477
O(1)	O(2)	1	0 -1 0	3.489
O(1)	C(5)	1	1 -1 0	3.493
O(2)	C(7)	2	0 0 0	3.385
O(2)	C(6)	2	-1 1 0	3.410
O(2)	O(2)	2	0 0 0	3.451

* Integers under this column refer to the following equivalent positions

1) x , y, z ;

2) -x, -y, -z ;

3) -x, - 1/2 + y , - 1/2 - z .

** For any distance the triple set of integers given under this column indicate the unit-cell translation that must be added to the appropriate equivalent position to derive the co-ordinates of the atom under the column Atom B from those given in Table 3.3 .

TABLE 3.9

Displacements (in Å) of atoms from the mean planes through

(a) all atoms ;

(b) aromatic carbon atoms C(1) to C(6) ;

(c) C(1) , C(7) , O(1) and O(2) .

Atom	(a)	(b)	(c)
F	0.076	0.002	0.427
O(1)	-0.177	-0.220	0.000
O(2)	0.156	0.181	0.000
C(1)	0.002	0.002	0.000
C(2)	0.030	-0.003	0.196
C(3)	0.029	0.003	0.180
C(4)	-0.015	0.000	-0.053
C(5)	-0.050	-0.001	-0.257
C(6)	-0.040	0.001	-0.230
C(7)	-0.011	-0.019	0.001

2.3.5 Discussion

In o-fluorobenzoic acid F...O and F...C(7) intramolecular distances are 2.608 and 2.832 Å respectively; while the sums of the corresponding normal van der Waals' radii are 2.75 and 3.35 Å respectively. This shows that the halogen substituent might have caused some strain in the structure.

The equation of the mean plane through the atoms of the molecule calculated by the method of Schomaker et al. (1959) is

$$0.3858X' + 0.9178Y - 0.0938Z' - 0.0151 = 0 \qquad (3)$$

where X', Y and Z' (in Å) are the orthogonal co-ordinates with reference to the orthogonal axes parallel to a^*, b and c. The root mean square (r.m.s.) distance of the atoms from the mean plane is 0.082 Å. The appropriate χ^2 test (See Sec. I, 1.8.5) shows that the atoms of the molecule are significantly non-planar. The displacements of the atoms from the mean plane are presented in Table 3.9(a). From this, it is evident that oxygen atoms O(1) and O(2) are displaced significantly towards the opposite sides of the mean plane (-0.177 and 0.156 Å respectively).

The best plane through the atoms of the benzene ring has the equation

$$0.3581X' + 0.9275Y - 0.1069Z' - 0.0297 = 0 \qquad (4)$$

The r.m.s. distance of these atoms from this mean plane is 0.0019 Å. The appropriate χ^2 test indicates that the benzene ring may be considered planar. Distances of the atoms from this mean plane are given in Table 3.9(b), which shows that to obtain more separation between them, the fluorine and the exocyclic carbon, C(7), are displaced in opposite direction from this mean plane. The extent of the deviation of the fluorine atom (0.002 Å) is negligible in comparison with that of C(7), (-0.019 Å). The corresponding displacements of halogen and exocyclic carbon atoms in o-chlorobenzoic acid and o-bromobenzoic acid (Ferguson and Sim, 1961, 1962a) are 0.036, -0.058 and 0.064, -0.057 Å respectively.

The equation of the mean plane through the aromatic carbon, C(1), and the carboxyl group atoms C(7), O(1) and O(2) is

$$0.5065X' + 0.8620Y - 0.0187Z' + 0.0062 = 0 \qquad (5)$$

The r.m.s. distance of these atoms from the mean plane is 0.0006 Å. Displacements of various atoms from this mean plane can be seen in Table 3.9(c). The dihedral angle between this plane and the aromatic plane (4) is 10.6° and is not far from the value of 8° obtained by Krausse (personal communications) from graphical work(in 1960). This rotation of the carboxyl group about the C(arom) - C(exocyclic) bond has considerably relieved the strain of overcrowding by increasing the intramolecular distance between the F and O(1) atoms. The comparable twists in o-chlorobenzoic acid and o-bromobenzoic acid (Ferguson and Sim, 1961, 1962 a) are 13.7 and 18.3° respectively. This shows that the extent of rotation between the carboxyl group plane and the aromatic plane, in o-halogeno-benzoic acids is increased with the increasing size of the halogen atom. The other usual way of relieving the strain of intramolecular overcrowding, in such circumstances, the distortion of the valency angles

$$F - \widehat{C(2)} - C(1), \quad C(2) - \widehat{C(1)} - C(7) \text{ and } C(1) - \widehat{C(7)} - O(1),$$

is not prominent in o-fluorobenzoic acid (Fig. 3.4).

The aromatic carbon-fluorine bond length, 1.330 Å, is similar to the average standard value of 1.30 ± 0.01 Å (Int. Tables, Vol. III, 1962). The carbon oxygen bond lengths of 1.223 and 1.260 Å are not far from those of 1.24 and 1.29 Å in benzoic acid (Sim, Robertson and Goodwin, 1955) and may be compared with those of 1.220 and 1.294 Å in 2-chloro-5-nitrobenzoic acid (Ferguson and Sim, 1962 b). The exocyclic C(1) - C(7) bond length of 1.463 Å is similar to 1.474 Å in o-chlorobenzoylacetylene (Chapter I).

An examination of the anisotropic temperature factors shows that the molecules of o-fluorobenzoic acid are under libration, but due to the dimer formation (Fig. 3.2), the movement is complex as a result of which the application of libration corrections is very difficult; the shortening of the mean value of the C - C bonds in the benzene ring (1.37 Å) may be attributed to this effect.

The shortest intermolecular contact occurs between the oxygen atom of the carboxyl group of one molecule, through the hydrogen bond to the hydroxyl group of another molecule. The OH...O distance of 2.583 Å may be compared with those of o-chloro-

benzoic acid (2.63 Å), o-bromobenzoic acid (2.64 Å) and benzoic acid (2.64 Å).

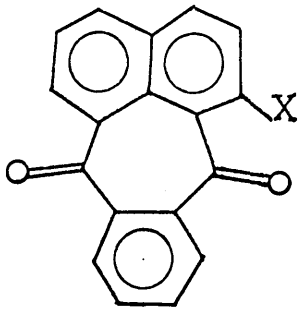
All other intermolecular separations (Table 3.8) are longer than the sums of the corresponding usual van der Waals' radii.

CHAPTER 4

2-CHLORO-1,8-PHTHALOYLNAPHTHALENE

2.4 INTRODUCTION

Eglinton and his collaborators have been carrying out a study of the infra-red absorption spectra of some o-halogeno-aroyl-compounds. (Brand, Eglinton and Morman, 1960; Brand, Eglinton and Tyrrell, 1965; Eglinton, Glasby and Lawrie (1966) and Eglinton, Ferguson, Islam and Glasby, 1967). During the investigations of some phthaloylnaphthalenes (I, II and III) they found that while the



(I) X = H

(II) X = OH

(III) X = Cl

unsubstituted compound (I) has a single carbonyl frequency in cyclohexane solution, the 2-hydroxy compound (II) has one unperturbed band at about the same frequency and one 42 $cm.^{-1}$ to lower frequency (-OH...O=C $<$, intra) and the 2-chloro compound (III) has one unperturbed band and a second band, but this time the latter is 32 $cm.^{-1}$ to higher frequency. The corresponding

values for chloroform solution and solid state show the same effects. From further studies of the i.r. spectra, it was assumed that some unusual steric effect must operate in the structure of 2-halogeno-1, 8-phthaloylnaphthalene. To provide detailed information on its molecular conformation, the x-ray crystal structure analysis of 2-chloro-1, 8-phthaloylnaphthalene was carried out.

2.4.1 Crystal data

2-Chloro-1, 8-phthaloylnaphthalene, $C_{18}H_9O_2Cl$, M = 292.5, m.p. = 145°C., monoclinic, a = 3.97 ± 0.02, b = 29.83 ± 0.04, c = 11.12 ± 0.03 Å, β = 101.6 ± 0.2°, U = 1291 Å^3, Z = 4, Dm = 1.50 gm/cc. (by flotation), Dc = 1.504 gm/cc., F(000) = 600; linear absorption coefficient for x-rays (λ = 1.542 Å), μ = 26.6 cm.$^{-1}$; space group $P2_1/c$ (C_{2h}^5, No.14, Int. Tables Vol. I, 1965).

Crystallisation from a petrol and acetone mixture afforded lath shaped crystals, elongated along the a-axis. From the intensity pattern in the a-axis oscillation and 0kℓ Weissenberg photographs it was evident that the crystal belonged to the monoclinic system. The cell constants were measured from oscillation, equatorial Weissenberg and precession photographs.

The 0kℓ to 3kℓ Weissenberg photographs and the precession photograph of the (h0ℓ) reciprocal lattice net were examined thoroughly and it was found that reflections were absent in h0ℓ spectra if ℓ was odd and 0k0 while k was odd. There was no restriction on general hkℓ reflections. Therefore, the space group is $P2_1/c$. (C_{2h}^5, No.14, Int. Tables Vol I, 1965).

2.4.2 Intensity data

For the collection of the intensity data, a small lath, which extinguished distinctly under the polarising microscope, was chosen. The reciprocal lattice nets 0kℓ to 3kℓ were then surveyed by equi-inclination Weissenberg methods using Cu Kα radiation ($\lambda = 1.542$ Å). For each set of the photographs, a six film-pack was used (Robertson, 1943). The intensities of 1217 independent reflections were measured by visual comparison with a calibrated intensity wedge. Out of these, 289 were "unobserved" but were included in all calculations and each was assigned half the value of the minimum intensity locally observable. By comparing the time of exposure for each set of Weissenberg photograph , all the 4 layers of intensity data were brought, approximately, on to the same scale. The intensity data were then corrected for appropriate Lorentz, polarisation and rotation factors (See Sec. I, 1.3.3). Considering the small size of the crystal, the absorption corrections were ignored.

The ratio of the square of the atomic number of the heavy atom to the sum of the squares for the light atoms per asymmetric unit is

$$\gamma = \frac{f_{Cl}^2}{\Sigma f_R^2} = 0.37 \qquad (1)$$

This indicates that the heavy atom method of phase determination for this structure may not be very promising (Sec. I, 1.6.3).

2.4.3 Structure determination and refinement in (100) projection

Due to the short a-axis (3.97 Å), it was expected that the structure would be clearly revealed in the (100) projection. While the three dimensional data collection was in progress, an attempt was made to solve the structure in this projection.

The Patterson synthesis for the (100) projection was computed with 195 0kℓ data. In the resulting map, the peaks corresponding to Cl-Cl vectors were not immediately obvious. To achieve better resolution, the intensity data were sharpened with respect to point chlorine atoms (Lipson and Cochran, 1966). In the projection of the sharpened Patterson function (Fig. 4.1), the peak 'A' was initially assumed to be the Cl-Cl general vector peak at (2y, 2z). Two copies of the map of the unsharpened Patterson projection were prepared on tracing paper in different colours. The heavy atom general vector peak (A) of one map

was then superimposed on the origin of the other and a minimum function map was prepared by drawing the minimum contour of the coincident peaks (Buerger, 1951); it did not reveal any chemically sensible structure. This indicated that peak 'A' might not be the genuine location of the Cl-Cl vector peak. On further investigation, peak 'B' was chosen as the desired peak situated at $2y = 0.5$. The minimum function map, based on this peak, revealed the whole structure (Fig. 4.2); because the heavy atom is at $y = 0.25$, the map possessed additional mirror symmetry which made its interpretation awkward. However, the approximate y and z co-ordinates for all the non-hydrogen atoms, except C(4) and C(16), were obtained from this map (for numbering scheme see Fig. 4.6). Structure factors based on the 19 atoms were then computed; the residual, R, at this stage, was 0.46. In the resulting electron density distribution, all the atoms, except O(1) and C(17), were well resolved. The approximate positional parameters for these two unresolved atoms were chosen by inspection and improved co-ordinates for the remaining atoms were calculated using Booth's method (Booth, 1948a). In the next cycle of structure factor

calculation, the R factor dropped to 0.26. In all the above structure factor calculations one isotropic temperature factor (Uiso = 0.044 $\AA^2$) was assigned to the non-hydrogen atoms and the intensity data were scaled so that $K \sum |F_o| = \sum |F_c|$ for the data.

The structure was then refined by the "Minimum Residual" method (Bhuiya and Stanley, 1963 ; Muir, 1966). In each cycle of the refinement, adjustments to the y and z co-ordinates and isotropic thermal parameters of the non-hydrogen atoms were made and an overall scale factor was also refined. After 6 cycles of the refinement, the residual, R, was 0.14.

Three cycles of full matrix least squares refinement led to no appreciable change in the positional parameters, but a slight adjustment of the isotropic thermal parameters and the scale factor was observed.

2.4.4 Structure solution in three dimensions

When the three dimensional data were available, the Harker section at v = 0.5 was calculated; it contained one dominating peak (Fig. 4.3), which led to the same z co-ordinate for the

Cl atom as had been determined from the projection work and also gave the x co-ordinate for the Cl atom.

Because its y co-ordinate is so near to 0.25, the Cl atom makes little or no contribution to the hkℓ planes with $\ell = 2n + 1$. Accordingly for the first three dimensional electron density calculation, all the 195 0kℓ planes, correctly phased from the projection work, were used along with those 1kℓ to 3kℓ data, with ℓ even, phased by the heavy atom contribution. Had Cl phasing alone been employed, complete mirror symmetry would have prevailed in the resulting electron density distribution. The strategy outlined above, had the effect of modulating the columns of electron density from the correctly phased 0kℓ data with the selected chlorine-phased upper layer data.

In the three dimensional electron density distribution 14 (out of the 21) non-hydrogen atoms were clearly revealed; the remainder were not sufficiently resolved in the x-direction. The x co-ordinates for these atoms were calculated and structure factors were computed with all (1217) planes for the 14 atoms using these x co-ordinates and (y, z) co-ordinates derived from the projection work. The residual, R, was 0.406. In the following

electron density distribution, peaks corresponding to all the 21 heavier atoms were clearly resolved. Structure factors were then calculated using all 21 atoms with x co-ordinates from this map and refined y and z co-ordinates from the (100) projection. The R factor was 0.229. After one further cycle of Fourier synthesis and structure factor calculation the residual, R, became 0.21.

To minimise the series termination error, two three dimensional electron density distributions were then computed— one with the F_o as Fourier coefficients and the other with F_c and hence the co-ordinates, corrected for the series termination errors (Booth, 1946 b) were computed (See Sec. I, 1.7.1.1). Structure factors were then computed for all 1217 planes using the co-ordinates corrected for series termination errors, and the refined isotropic thermal parameters derived from the projection work. The intensity data were then scaled so that $K\Sigma|F_o| = \Sigma|F_c|$ for each layer. No later alterations of these layer scales were found necessary; only an overall scale factor was subsequently refined.

The course of the structure solution is shown in Table 4.1.

2.4.5 Structure refinement in three dimensions by least squares methods

Altogether 13 cycles of least squares refinement were carried out, at the end of which the refinement was converged. In all stages of the refinement, a block diagonal approximation to the normal equations was used. The progress of the refinement can be seen in Table 4.2. The final R factor is 0.097.

In the first three cycles of the refinement an overall scale factor, isotropic thermal and positional parameters for the non-hydrogen atoms were adjusted. The weighting scheme employed, was that of Cruickshank et al. (1961),

$$\sqrt{w} = 1/(p_1 + |F| + p_2 |F|^2)^{\frac{1}{2}} \qquad (2)$$

Initially the constant p_1 and p_2 were chosen as $2|F|_{min}$ and $2/|F|_{max.}$ (Cruickshank, 1964), i.e. 8 and 0.025 repectively and until the final stage of refinement, no further adjustment of the values of these constants was made.

Since, the available least squares program could not adjust individual layer scale factors, these were occasionally checked by comparing $\Sigma|F_o|$ with $\Sigma|F_c|$ for each layer.

After the third cycle of refinement, a difference synthesis was computed. In this map there were indications of anisotropic vibrations and peaks corresponding to the hydrogen atoms were revealed, no other significant features were noticed. The refinement was then continued for the adjustment of an overall scale factor, anisotropic thermal and positional parameters for the 21 non-hydrogen atoms. At the end of the sixth cycle of the least squares refinement, the residual, R, was 0.146. Peaks of the 9 hydrogen atoms were clearly revealed in the difference synthesis. Because of the uncertainty in locations of the maxima, the positions of the hydrogen atoms were calculated assuming normal distances and angles (Int. Tables, Vol. III, 1962). In the subsequent cycles of least squares, the contributions of the hydrogen atoms were included using these calculated positional parameters and isotropic temperature factors equal to those of adjacent carbon atoms. Neither the positional nor the thermal parameters of the hydrogen atoms were refined.

On a thorough examination of the agreement between $|F_o|$ and $|F_c|$, two high order reflections were found to be misindexed.

Half a dozen of the very low order strong reflections were seen to exhibit very bad agreement. These were independently re-estimated and an approximate spot shape corrections were made and the least squares refinement was continued.

After further three cycles of refinement, the weighting analysis was checked to ensure that average $\Sigma w\Delta^2$ for all batches of the data grouped in the order of increasing $|F_o|$ and $\sin\theta/\lambda$ values were similar. To achieve better agreement, the values of the constants (p_1 and p_2) were finally adjusted to 15 and 0.023 respectively.

After the thirteenth cycle of refinement, the parameter shifts were quite negligible and in any case less than one third of the corresponding estimated standard deviations indicating the convergence of the refinement. Structure factors were then calculated including only the contributions of the non-hydrogen atoms. In the resulting difference synthesis, peaks corresponding to the hydrogen atoms were clearly revealed. The relevant sections parallel to (100) projection are shown in Fig. 4.4, along with the three dimensional electron density distributions for all the 21 atoms. There were no other significant features in the difference

map confirming that the refinement was completed.

In the structure factor calculations, the atomic scattering curves used were of Int. Tables, Vol. III (1962).

2.4.6 Final atomic parameters, molecular dimensions etc.

A view of the buckled molecule is shown in a special projection in Fig 4.5. Bond lengths, valency angles and the numbering scheme used for identifying the atoms of a molecule can be seen in Fig. 4.6. The molecular packing viewed down the a-axis is presented in Fig. 4.7.

The agreement of the calculated and observed structure factors is shown in Table 4.3. The fractional co-ordinates of the non-hydrogen atoms with their estimated standard deviations are given in Table 4.4 and the corresponding orthogonal co-ordinates, referred to the axes parallel to a^*, b and c, along with the estimated standard deviations are in Table 4.5. In Table 4.6, there are the calculated fractional co-ordinates for the hydrogen atoms and their (assumed) isotropic temperature factors, Uiso. The anisotropic thermal parameters of the 21

heavier atoms and their estimated standard deviations can be seen in Table 4.7 in terms of values of U_{ij} (See Sec. I, 1.3.2). Principal values and the direction cosines of the vibration tensors, with reference to the orthogonal axes parallel to a*, b and c, are presented in Table 4.8 and deviations of atoms from various mean planes are in Table 4.9. Some short intramolecular and intermolecular contacts are given in Table 4.10.

The average estimated standard deviations of carbon-carbon, carbon-oxygen and carbon-chlorine valency bonds are 0.010, 0.008 and 0.007 $\mathring{A}$ respectively. The mean estimated standard deviation of the valency angles is 0.6°.

DIAGRAMS AND TABLES

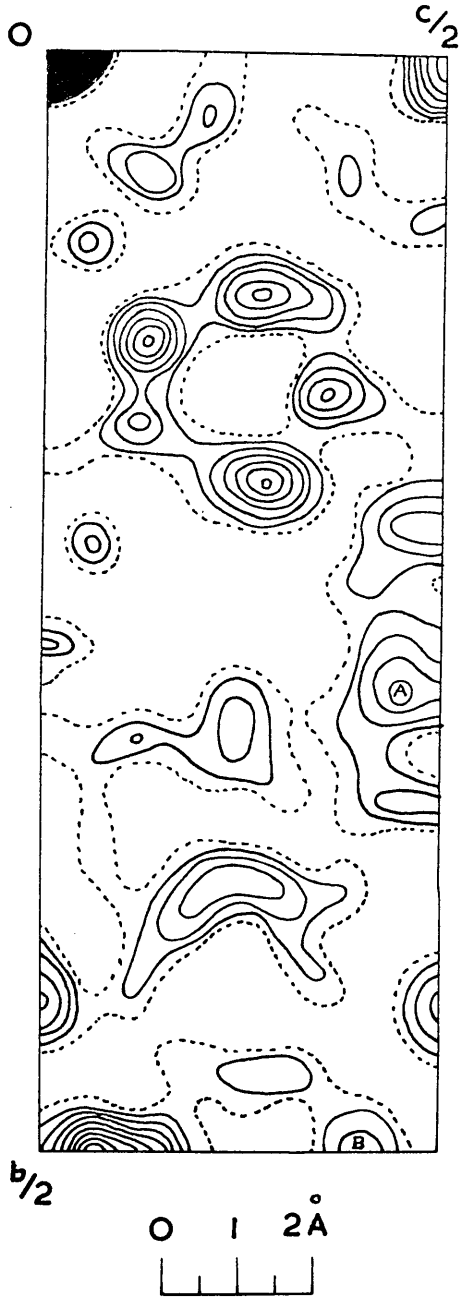


FIG. 4.1

The Patterson synthesis in the (100) projection. Contours are at arbitrary intervals.

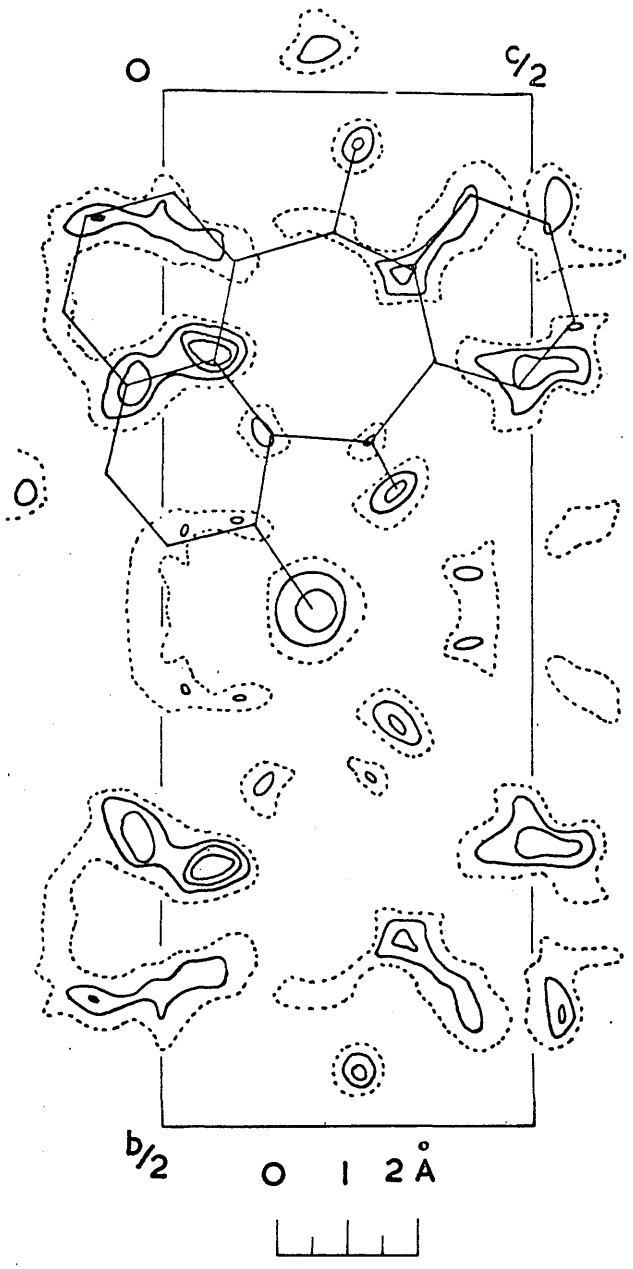


FIG. 4.2

The minimum function in projection on (100) obtained from superimposition of the Cl-Cl vectors in (100) Patterson projection and its interpretation.

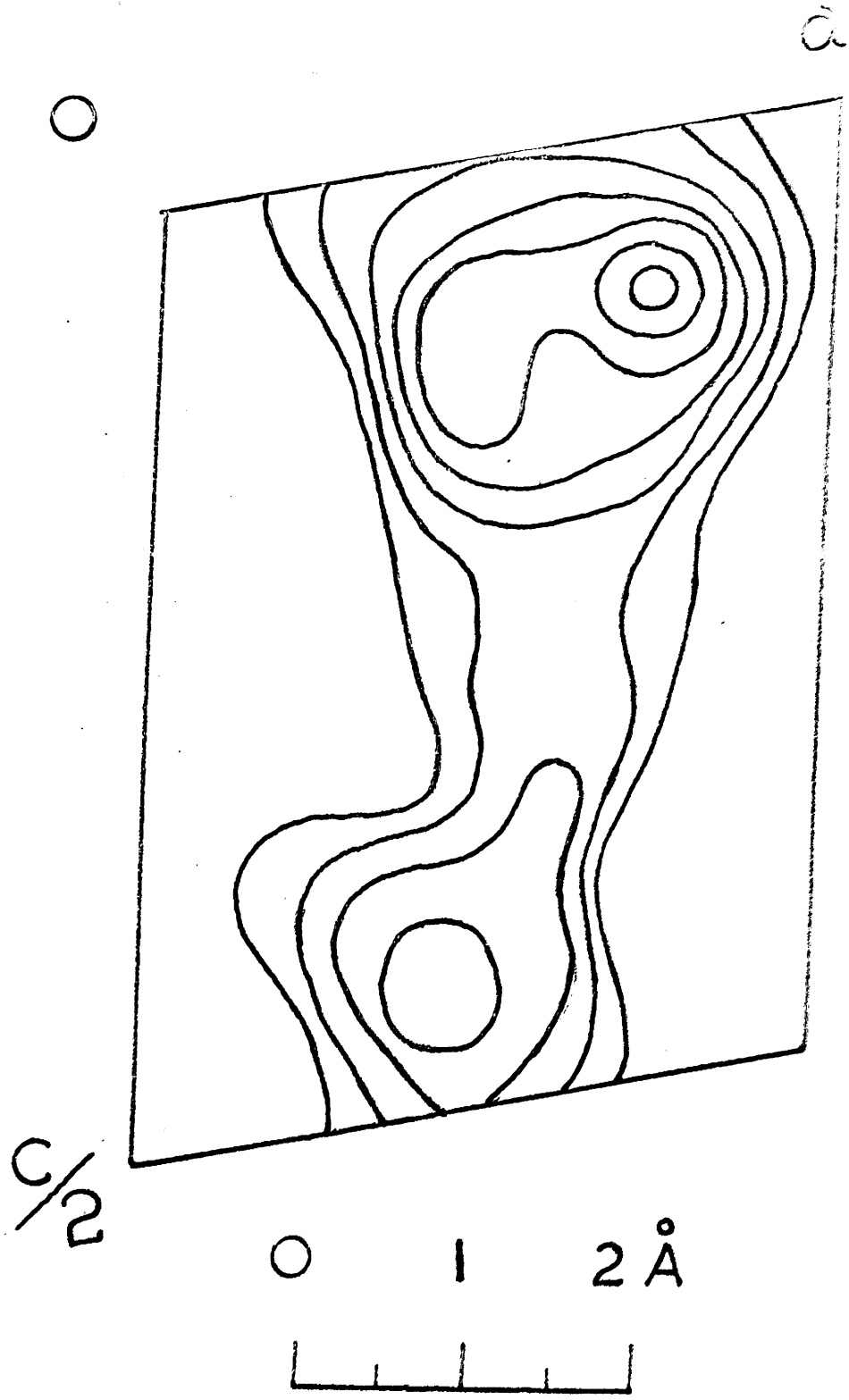


FIG. 4.3

The Harker section at v = $\frac{1}{2}$. Contours are at arbitrary intervals.

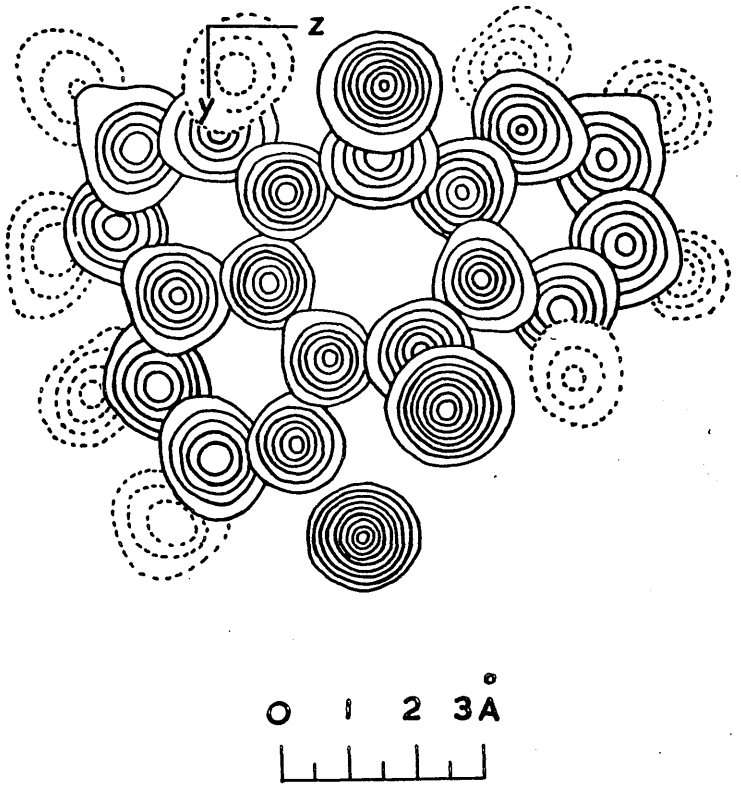


FIG. 4.4

The third electron density distribution (solid contours) shown by means of superimposed contour sections parallel to (100). Also shown are the hydrogen peaks (broken contours) found in the difference synthesis computed at the conclusion of the refinement. Contour levels are at 0.1 e/$Å^3$ around the hydrogen atoms starting at 0.6 electron level. For other atoms contour levels are at 1 e/$Å^3$ except around Cl(2 e/$Å^3$) starting at the one electron level.

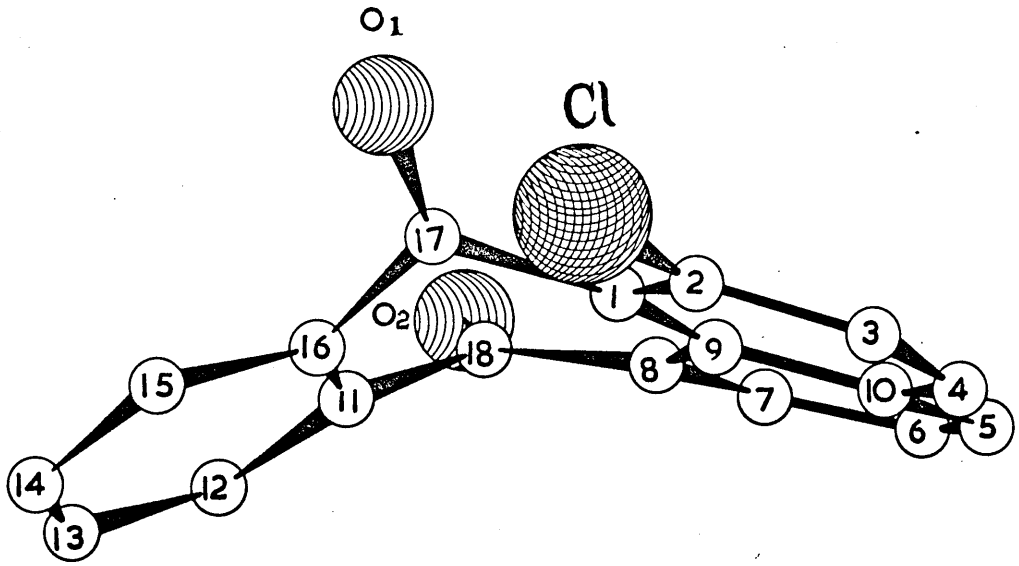


FIG. 4.5

A special view of the buckled molecule

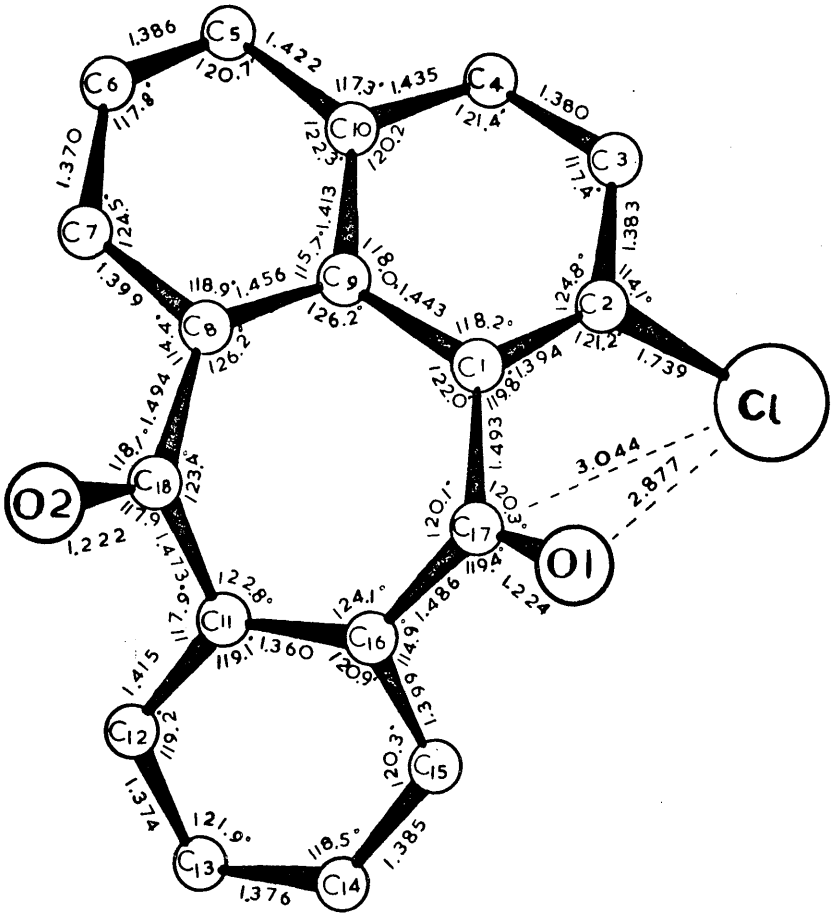


FIG. 4.6

The molecular diagram showing the bond-lengths (in Å), the valency angles (in degrees) and the numbering scheme used for the non-hydrogen atoms of a molecule. The hydrogen atoms have the same numbering system as the carbon atoms to which they are bonded.

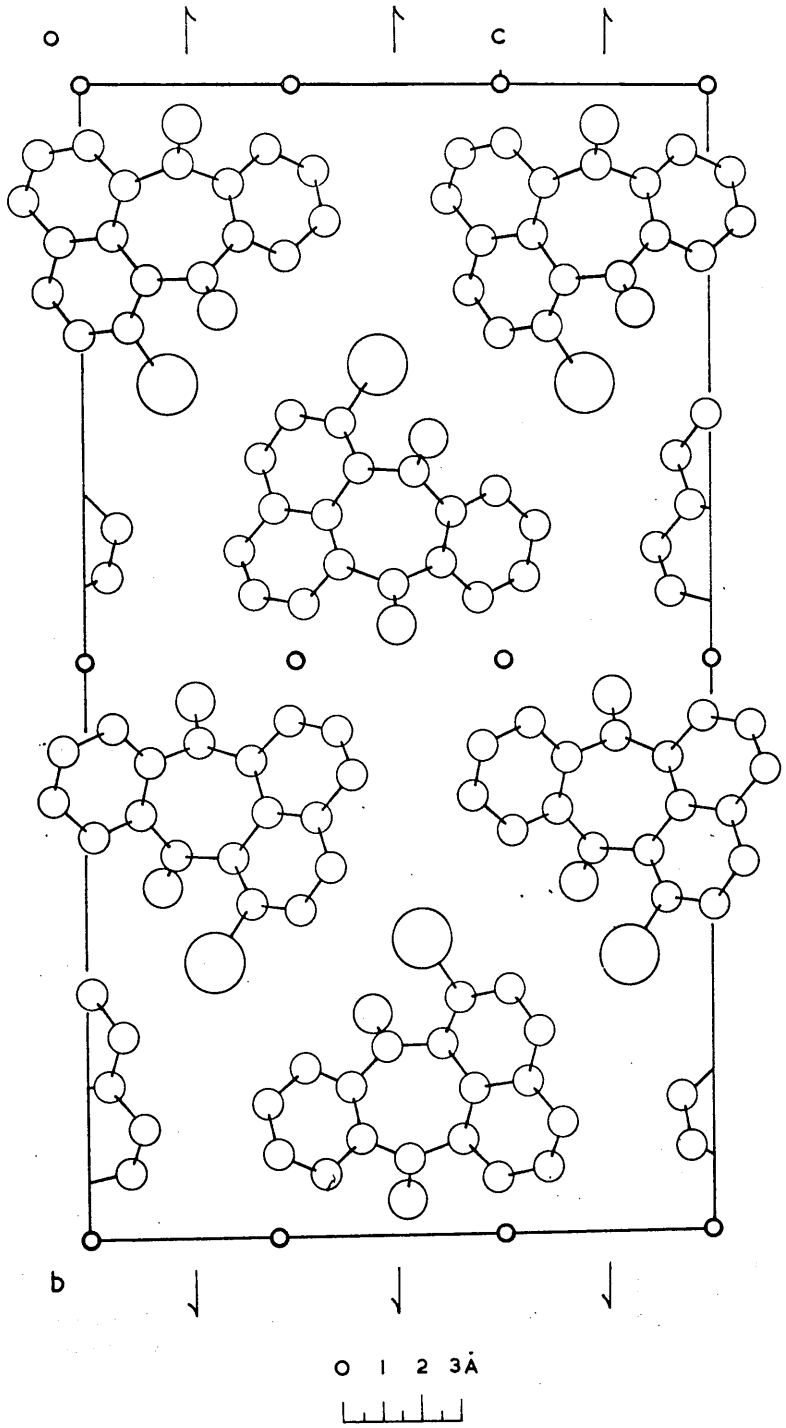


FIG. 4.7

The molecular packing viewed down the short a-axis.

TABLE 4.1

COURSE OF THE STRUCTURE ANALYSIS

The analysis in (1 0 0) projection

OPERATION	ATOMS INCLUDED	R FACTOR
Patterson synthesis.	Cl	-
Minimum function map.	All non-hydrogen atoms except C(14) and C(16).	-
Structure factor calculation and electron density synthesis.	All the 21 non-hydrogen atoms.	0.46
Structure factor calculation.		0.26
6 Cycles of refinement by minimum residual method.	Improved locations of all the 21 atoms.	0.14

The analysis in three dimensions

Harker section at v = 0.5 .	Cl	-
Structure factor calculation and elecron density synthesis with selected planes.	Cl,O(1),O(2),C(1) to C(10) and C(17) .	0.62
Structure factor calculation and electron density synthesis with full data.	All the 21 non-hydrogen atoms.	0.41
-Do-	Improved locations of all the 21 atoms.	0.23
Structure factor calculation.		0.21

TABLE 4.2

PROGRESS OF THE REFINEMENT

Cycle No.	R factor	$\Sigma w\Delta^2$	$R' = \Sigma w\Delta^2 / \Sigma w\|Fo\|^2$
1[a]	0.197	982	0.102
2	0.187	596	0.068
3	0.182	521	0.065
4[b]	0.181	511	0.064
5	0.154	380	0.048
6	0.146	330	0.044
7[c]	0.146	252	0.042
8	0.101	93	0.017
9	0.099	90	0.016
10[d]	0.099	91	0.017
11	0.097	80	0.016
12[e]	0.097	64	0.015
13	0.097	64	0.014

a) Refinement of overall scale factor, isotropic thermal and positional parameters .

b) Refinement continued with anisotropic thermal vibrations .

c) Re-estimation of a few planes and inclusion of H atoms .

d) Adjustment of the weighting scheme .

e) Further adjustment of the weighting scheme .

TABLE 4.3

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	|Fo|	Fc
0	0	2	14.1	11.2
0	0	4	6.4	-4.9
0	0	6	6.8	-7.5
0	1	2	5.2	-6.7
0	1	3	3.4	-2.0
0	1	4	14.9	16.6
0	1	5	17.4	-16.0
0	1	6	6.8	-7.3
0	1	7	3.7	1.2
0	1	8	12.6	15.4
0	1	9	11.2	12.7
0	2	2	78.8	-80.8
0	2	3	36.8	38.1
0	2	4	33.1	30.2
0	2	5	2.6	3.0
0	2	6	18.4	19.6
0	2	8	34.2	-35.8
0	2	7	3.7	3.3
0	2	8	15.7	15.3
0	2	9	17.7	-17.9
0	3	2	48.7	51.8
0	3	3	20.0	-22.2
0	3	4	46.2	47.9
0	3	5	39.5	39.4
0	3	6	7.2	-6.4
0	3	7	3.7	2.1
0	3	8	4.1	3.0
0	4	0	44.6	-46.8
0	4	1	4.1	4.0
0	4	2	76.1	-73.4
0	4	3	18.1	18.5
0	4	4	51.6	53.3
0	4	5	35.3	-39.1
0	4	6	10.9	10.2
0	4	7	7.5	4.7
0	5	1	28.3	33.8
0	5	2	35.3	-36.6
0	5	3	30.2	30.7
0	5	4	39.4	37.8
0	5	5	16.3	-16.7
0	5	6	36.4	-37.1
0	5	7	9.4	9.0
0	5	8	4.1	4.3
0	5	9	4.4	-5.4
0	6	0	15.5	-16.0
0	6	1	70.4	-66.8
0	6	2	41.4	-40.7
0	6	3	12.1	11.5
0	6	4	19.8	17.7
0	6	5	10.9	1.8
0	6	6	20.9	-21.3
0	6	7	23.1	-23.0
0	7	1	49.1	49.9
0	7	2	14.6	-14.5
0	7	4	7.4	-7.7
0	7	5	15.1	13.9
0	7	6	34.6	36.3
0	7	7	17.8	-17.3
0	7	8	26.1	-25.5
0	7	9	24.3	-26.7
0	7	10	11.9	-13.4
0	8	0	34.0	-31.1
0	8	1	45.5	44.9
0	8	2	12.0	-11.9
0	8	3	28.8	30.9
0	8	4	3.9	4.5
0	8	5	26.7	-25.8
0	8	6	2.8	2.5
0	8	7	8.4	-7.4
0	9	1	5.0	5.2
0	9	2	35.8	-32.2
0	9	3	31.9	33.7
0	9	4	51.3	53.5
0	9	5	3.3	2.3
0	9	6	17.6	-17.4
0	9	7	3.9	4.3
0	10	0	70.7	-66.3
0	10	1	36.0	33.2
0	10	2	6.9	7.6
0	10	3	29.5	-29.5
0	10	4	48.1	-47.5
0	10	5	15.4	-16.3
0	10	6	3.7	2.9
0	10	7	20.2	19.6
0	11	1	4.1	-3.7
0	11	2	19.9	19.1
0	11	3	26.0	-24.8
0	11	4	50.6	-47.3
0	11	5	13.9	-13.3
0	11	6	14.9	15.9
0	11	7	4.1	-1.5
0	11	8	9.1	8.6
0	12	0	3.7	3.6
0	12	1	33.5	-33.1
0	12	2	58.2	-54.3
0	12	3	24.1	25.0
0	12	4	8.8	-8.1
0	12	5	6.1	5.7
0	12	6	16.4	15.7
0	13	1	14.0	-13.6
0	13	2	11.9	-11.1
0	13	3	8.1	-6.9
0	13	4	14.8	14.8
0	13	5	17.7	-17.2
0	13	6	13.3	-14.1
0	14	0	16.3	-15.2
0	14	1	13.7	13.6
0	14	2	54.3	55.6
0	14	3	3.9	4.6
0	14	4	3.5	-2.2
0	14	5	3.7	1.2
0	14	8	12.1	12.0
0	15	1	3.1	-3.3
0	15	2	3.2	4.9
0	15	3	3.4	4.1
0	15	4	22.0	-21.7
0	15	5	11.0	9.3
0	15	6	19.2	18.9
0	15	7	19.2	-19.3
0	15	8	9.4	6.5
0	16	0	39.9	35.9
0	16	1	39.3	-39.5
0	16	2	3.3	3.3
0	16	3	7.4	-6.4
0	16	4	3.7	-2.8
0	16	5	14.4	13.4
0	16	6	4.2	-6.3
0	16	7	11.7	10.7
0	16	8	21.7	-19.0
0	17	1	5.9	-5.3
0	17	2	3.5	-3.7
0	17	3	8.1	10.5
0	17	4	3.8	3.7
0	17	5	4.0	4.3
0	17	6	12.0	-12.4
0	17	7	9.6	10.1
0	17	8	16.3	16.6
0	18	0	30.0	-28.1
0	18	1	20.6	18.8
0	18	2	26.2	-23.5
0	18	3	3.7	-2.7
0	18	4	3.9	3.8
0	18	5	7.7	7.9
0	19	1	16.3	15.2
0	19	2	3.7	4.1
0	19	3	24.6	-23.5
0	19	4	4.0	-5.7
0	19	5	14.1	13.0
0	19	7	9.4	10.9
0	19	8	12.2	-13.6
0	20	0	3.8	-0.9
0	20	1	13.3	-11.8
0	20	2	3.7	-2.4
0	20	3	10.6	15.3
0	20	4	4.1	6.8
0	20	5	6.4	-7.1
0	20	6	15.3	13.6
0	20	7	9.4	-6.7
0	21	1	11.0	10.7
0	21	2	4.0	4.9
0	21	3	24.9	22.9
0	21	4	13.2	11.1
0	21	5	15.6	-16.2
0	22	0	14.9	14.9
0	22	1	37.1	33.7
0	22	2	22.0	21.5
0	22	3	6.7	-7.9
0	22	4	11.2	-12.0
0	22	5	10.4	9.5
0	23	1	24.5	22.6
0	23	2	20.9	20.5
0	23	3	4.3	-3.1
0	23	4	4.4	3.6
0	23	5	12.9	13.7
0	24	0	21.2	21.0
0	24	1	8.6	-6.4
0	24	2	5.7	-6.2
0	24	3	4.4	-4.3
0	24	4	11.7	-11.0
0	25	1	12.0	-11.4
0	25	2	4.4	-7.0
0	25	3	14.8	14.1
0	25	4	4.4	6.8
0	25	5	14.2	-12.0
0	26	1	4.4	5.2
0	26	2	4.4	4.1
0	26	3	20.8	-20.0
0	26	4	4.4	4.3
0	27	1	4.4	-3.4
0	27	2	4.4	1.9
0	27	3	15.0	-13.4
0	27	4	15.8	-14.8
0	27	5	11.5	11.7
0	28	0	21.1	17.8
0	28	2	20.2	19.8
0	28	3	21.9	24.7
0	28	4	18.5	-21.4
0	28	6	13.7	16.6
1	1	1	42.8	-41.6
1	1	3	43.6	44.4
1	1	2	25.3	25.6
1	1	1	31.7	-33.0
1	1	-2	40.6	-44.2
1	1	-3	25.3	-26.2
1	1	-4	27.0	31.7
1	1	-5	21.6	20.7
1	1	-6	6.1	-7.4
1	2	6	17.0	-18.5
1	2	5	7.7	-7.7
1	2	4	50.7	53.4
1	2	3	26.4	-24.9
1	2	2	64.5	-66.8
1	2	1	116.2	-116.2
1	2	-2	41.2	39.6
1	2	-3	9.5	-10.7
1	2	-4	13.4	-15.1
1	2	-5	2.3	3.2
1	2	-6	6.2	8.1
1	3	8	10.3	9.7
1	3	7	10.3	9.5
1	3	6	14.9	-12.3
1	3	5	9.4	8.4
1	3	4	2.3	2.3
1	3	3	23.8	-22.2
1	3	2	46.7	46.0
1	3	1	26.3	26.6
1	3	-1	10.3	10.7
1	3	-2	32.1	-37.1
1	3	-3	6.5	5.7
1	3	-4	2.6	-3.3
1	3	-7	13.1	-14.2
1	4	7	3.2	-6.0
1	4	6	8.6	8.8
1	4	5	18.7	18.9
1	4	4	5.2	-3.3
1	4	3	2.7	4.6
1	4	2	40.7	-40.1
1	4	1	34.9	33.2
1	4	0	20.6	-18.2
1	4	-1	33.8	31.5
1	4	-2	21.1	19.7
1	4	-3	51.7	51.0
1	4	-5	2.3	3.8
1	4	-6	28.1	-32.0
1	4	-7	18.5	-21.2
1	5	8	3.2	-5.8
1	5	7	3.3	5.0
1	5	6	7.8	8.3
1	5	5	7.3	8.1
1	5	4	2.4	2.3
1	5	3	13.7	13.6
1	5	2	10.2	-10.8
1	5	1	40.1	-39.3
1	5	0	1.5	0.8
1	5	-3	29.9	-27.4
1	5	-4	2.1	2.4
1	5	-5	25.7	-27.7
1	5	-6	11.4	-14.5
1	5	-7	3.0	3.8
1	6	8	19.1	-21.5
1	6	7	16.7	16.2
1	6	6	12.5	-10.3
1	6	5	15.3	-15.3
1	6	4	11.2	11.9
1	6	3	10.4	9.9
1	6	2	31.7	-29.1
1	6	1	10.7	-10.1
1	6	-1	16.3	-13.3
1	6	-2	42.0	-42.6
1	6	-5	5.1	3.8
1	6	-6	14.3	16.1
1	6	-7	25.0	29.2
1	7	7	10.4	13.2
1	7	6	10.9	-11.7
1	7	5	10.9	-11.7
1	7	4	14.1	17.0
1	7	3	18.1	15.8
1	7	2	23.1	19.5
1	7	1	6.7	6.2
1	7	0	9.6	-9.1
1	7	-1	8.0	8.9
1	7	-3	5.5	-7.0
1	7	-4	36.1	33.5
1	7	-5	19.1	19.5
1	7	-7	56.5	-54.5
1	8	7	9.3	-8.3
1	8	6	50.1	53.1
1	8	5	2.0	1.2
1	8	4	7.4	7.9
1	8	3	9.6	-11.7
1	8	2	13.0	15.6
1	8	1	3.1	1.2
1	8	0	6.4	8.6
1	8	-1	3.5	6.2
1	8	-2	9.0	-10.4
1	8	-3	10.4	10.1
1	8	-4	10.4	9.4
1	8	-5	9.0	-8.5
1	8	-6	24.0	-24.1
1	8	3	2.3	-2.1
1	8	2	33.3	30.5
1	8	1	1.9	-3.5
1	8	0	51.8	-52.4
1	8	-1	18.2	16.8
1	8	-2	35.3	31.6
1	8	-3	13.4	-13.1
1	8	-4	17.0	-18.8
1	8	-5	34.4	38.3
1	8	-6	19.2	-24.2
1	8	-7	3.1	-2.8
1	8	-8	21.9	25.3
1	8	-9	7.9	-8.9
1	9	8	20.4	-19.7
1	9	7	25.1	-20.4
1	9	6	13.6	11.9
1	9	5	4.6	-5.3
1	9	4	2.6	1.2
1	9	3	2.4	-2.8
1	9	2	2.2	2.0
1	9	1	26.0	-25.3
1	9	0	52.0	45.1
1	9	-1	20.4	18.9
1	9	-2	16.2	-17.7
1	9	-3	10.7	-12.7
1	9	-4	10.1	10.2
1	9	-5	14.5	16.7
1	9	-6	13.7	14.6
1	10	7	14.2	-14.0
1	10	6	3.3	-1.2
1	10	5	14.6	-16.5
1	10	4	17.7	16.7
1	10	3	37.9	34.2
1	10	2	6.1	4.9
1	10	1	2.1	-1.7
1	10	0	2.0	3.7
1	10	-1	15.2	-14.1
1	10	-2	20.7	-18.1
1	10	-3	14.5	15.0
1	10	-4	29.2	-30.6
1	10	-5	9.7	-10.0
1	10	-6	17.2	20.8
1	10	-7	3.2	1.0
1	10	-8	9.8	-11.1
1	11	7	6.2	-6.6
1	11	6	30.6	-28.4
1	11	5	22.3	-19.2
1	11	4	7.0	-6.6
1	11	3	15.1	13.7
1	11	2	31.9	30.6
1	11	1	42.9	41.1
1	11	-1	8.1	-9.1
1	11	-2	27.5	29.0
1	11	-3	43.1	46.1
1	11	-4	40.2	-40.9
1	11	-5	2.8	1.7
1	11	-6	3.0	-1.9
1	11	-7	10.1	9.1
1	11	-8	7.1	7.0
1	12	5	30.0	28.2
1	12	4	13.9	-13.7
1	12	3	5.3	-4.3
1	12	2	43.1	41.9
1	12	1	17.3	15.8
1	12	0	10.0	10.1
1	12	-1	12.1	10.9
1	12	-2	3.7	5.2
1	12	-3	7.2	-7.8
1	12	-4	16.6	16.8
1	12	-5	12.4	14.0
1	13	7	9.8	-10.1
1	13	6	36.3	35.0
1	13	5	8.4	-9.0
1	13	4	11.1	-10.5
1	13	3	15.4	-14.5
1	13	2	41.7	-38.3
1	13	1	23.5	21.9
1	13	0	13.1	-11.6
1	13	-1	5.0	-5.1
1	13	-2	33.7	-33.7
1	13	-3	8.4	-9.7
1	13	-4	19.2	21.3
1	13	-5	6.8	8.9
1	14	7	7.7	6.8
1	14	6	3.4	-2.4
1	14	5	20.6	-18.7
1	14	4	10.0	8.8
1	14	3	21.2	19.8
1	14	2	37.7	-34.1
1	14	1	21.3	-20.4
1	14	0	3.9	1.2
1	14	-1	2.5	3.4
1	14	-2	7.7	7.9
1	14	-3	3.7	-1.9
1	14	-4	25.3	-26.8
1	14	-5	23.5	-23.2
1	14	-6	11.5	12.6
1	15	6	7.4	-7.9
1	15	5	16.3	14.7
1	15	4	6.9	-6.6
1	15	3	9.2	-9.5
1	15	2	2.8	1.0
1	15	1	9.0	-8.2
1	15	0	8.8	-8.4
1	15	-1	27.5	-28.8
1	15	-2	2.7	1.2
1	15	-3	8.5	7.2
1	15	-4	27.5	-27.5
1	15	-5	12.2	-13.0
1	15	-6	8.5	8.8
1	15	-7	7.9	8.5
1	15	-8	8.2	8.5
1	16	7	24.3	-22.2
1	16	6	29.5	25.2
1	16	5	3.4	-2.9
1	16	4	18.4	-17.6
1	16	3	21.6	-20.1
1	16	2	23.2	20.9
1	16	1	9.6	9.3
1	16	0	13.6	-13.9
1	16	-1	5.4	-7.2
1	16	-2	6.0	-7.1
1	16	-3	16.4	-18.3
1	16	-4	3.0	8.9
1	16	-5	3.2	-2.6
1	16	-6	12.3	-14.5
1	16	-7	9.6	-11.0
1	16	-8	10.6	10.8
1	17	6	12.2	-12.8
1	17	5	19.4	18.5
1	17	4	8.7	-7.9
1	17	3	12.5	-11.6
1	17	2	5.6	7.6
1	17	1	2.9	-3.4
1	17	0	17.7	18.6
1	17	-1	14.8	14.7
1	17	-2	16.8	-16.4
1	17	-3	3.0	4.4
1	17	-4	8.4	9.6
1	18	7	9.3	8.0
1	18	6	15.5	-12.2
1	18	5	3.5	-3.3
1	18	4	15.2	12.5
1	18	3	11.4	9.4
1	18	2	10.6	-9.9
1	18	1	22.5	-22.8
1	18	0	6.8	-7.2
1	18	-1	2.9	2.3
1	18	-2	5.3	6.7
1	18	-3	7.4	8.2
1	18	-4	3.2	3.2
1	18	-5	3.3	-2.1
1	18	-6	7.9	8.4
1	18	-7	3.6	5.0
1	18	-8	21.8	-20.4
1	19	7	13.3	13.1
1	19	6	3.6	-5.6
1	19	5	3.5	-1.1
1	19	4	7.8	7.2
1	19	3	9.2	-9.5
1	19	2	8.1	-8.6
1	19	1	12.5	12.6
1	19	0	3.1	4.9
1	19	-1	19.6	-21.2
1	19	-2	3.1	4.8
1	19	-3	20.0	24.6
1	19	-4	7.3	-8.0
1	19	-5	11.5	-12.8
1	20	4	20.5	18.3
1	20	3	11.3	-11.5
1	20	2	15.7	13.7
1	20	1	14.6	14.8
1	20	0	13.2	-13.4
1	20	-1	10.0	10.2
1	20	-2	15.6	15.6
1	20	-3	18.9	-19.5
1	20	-4	18.4	20.8
1	20	-5	13.2	14.0
1	21	5	17.3	15.0
1	21	4	14.8	14.0
1	21	3	10.1	8.2
1	21	2	3.4	-3.6
1	21	1	21.0	-19.7
1	21	0	8.0	7.6
1	21	-1	21.8	22.1
1	21	-2	3.3	-4.3
1	21	-3	18.8	-18.8
1	21	-4	18.5	19.7
1	21	-5	3.5	-4.1
1	21	-6	9.3	-9.7
1	22	2	7.7	-7.7
1	22	1	11.7	-10.9
1	22	0	3.4	3.5
1	22	-1	3.4	1.0
1	22	-2	8.6	9.0
1	22	-3	10.3	12.5
1	22	-4	17.4	-17.5
1	23	4	11.3	-10.4
1	23	3	14.7	11.2
1	23	2	8.7	9.9
1	23	1	3.9	-2.4
1	23	0	15.6	15.6
1	23	-1	38.9	-36.7
1	23	-2	21.4	19.3
1	23	-3	3.5	-4.8
1	23	-4	7.3	8.7
1	24	5	10.7	9.1
1	24	4	3.6	-4.6
1	24	3	18.0	-17.2
1	24	2	7.9	8.5
1	24	1	15.5	16.2
1	24	0	3.5	-4.9
1	24	-1	7.2	-7.9
1	24	-2	7.5	-9.0
1	24	-3	12.2	12.2
1	24	-4	9.5	-9.0
1	24	-5	7.2	7.6
1	25	4	16.9	-13.2
1	25	3	3.6	4.9
1	25	2	3.6	-1.3
1	25	1	3.6	4.8
1	25	0	22.9	24.1
1	25	-1	19.1	21.5
1	25	-2	15.0	-17.1
1	26	3	15.1	13.6
1	26	2	3.6	0.8
1	26	1	3.6	2.6
1	26	0	12.3	14.0
1	26	-1	9.1	9.8
1	26	-2	3.6	2.3
1	26	-3	9.6	10.8
1	26	-4	3.6	-5.9
1	26	-5	13.9	-13.2
1	27	3	12.2	-12.5
1	27	2	9.4	10.0
1	27	1	3.6	3.4
1	27	0	3.6	2.8
1	27	-1	3.6	4.7
1	27	-2	3.6	3.3
1	27	-3	11.1	11.0
1	28	3	15.5	-13.1
1	28	2	3.5	2.7
1	28	1	15.0	12.9
1	28	0	3.6	-5.9
1	28	-1	7.7	-8.4
1	29	1	8.3	-7.3
1	29	0	3.5	-2.1
1	29	-1	7.2	7.8
2	0	-2	7.6	7.5
2	0	-4	3.4	0.6
2	0	-4	11.1	9.0
2	0	-2	33.7	36.5
2	0	0	74.6	-73.9
2	0	2	3.2	-3.3
2	0	4	11.2	-11.3
2	0	6	10.9	11.4
2	1	-9	8.9	-7.2
2	1	-8	20.0	17.8
2	1	-7	3.6	-4.0
2	1	-6	13.5	-11.1
2	1	-5	2.3	1.5
2	1	-4	10.3	10.9
2	1	-3	1.5	-2.1
2	1	-2	3.3	10.6
2	1	-1	12.4	12.6
2	1	0	7.3	-8.4
2	1	1	29.2	26.7
2	1	2	57.0	53.2
2	1	3	12.6	11.7
2	1	4	5.2	5.0
2	1	5	8.3	-7.3
2	1	6	7.4	6.3
2	1	7	3.4	-4.4
2	1	8	8.9	10.1
2	2	-9	12.3	-10.7
2	2	-8	12.4	10.0
2	2	-7	10.1	-8.6
2	2	-6	6.4	-6.2
2	2	-5	2.9	3.0
2	2	-4	24.6	-24.1
2	2	-3	20.3	-22.7
2	2	-2	5.7	7.3
2	2	-1	16.7	-14.2
2	2	0	25.1	22.0
2	2	1	3.6	-3.9
2	2	2	6.4	-6.2
2	2	3	7.1	7.3
2	2	4	3.4	1.0
2	2	5	8.9	-9.9
2	3	-9	6.5	5.2
2	3	-8	3.2	-2.7
2	3	-7	8.0	-7.9
2	3	-6	29.3	28.5
2	3	-5	9.0	-8.7
2	3	-4	48.0	-48.9
2	3	-3	55.5	-54.1
2	3	-2	53.7	-52.7
2	3	-1	14.9	-14.0
2	3	0	43.1	44.6
2	3	1	5.3	-5.7
2	3	2	3.6	-3.7
2	3	3	11.6	11.6
2	3	4	13.6	12.1
2	3	5	7.5	-6.9
2	4	-9	10.8	11.0

TABLE 4.3 Cont.

H	K	L	|Fo|	Fo
2	4	-18	3.2	-2.0
2	4	-17	14.2	11.4
2	4	-16	12.2	8.5
2	4	-15	8.5	-7.6
2	4	-14	37.5	-34.2
2	4	-13	18.6	-17.8
2	4	-12	1.5	-0.4
2	4	-11	18.3	-17.8
2	4	-10	7.6	7.5
2	4	-9	13.3	-11.3
2	4	-8	27.1	26.9
2	4	-7	16.6	17.7
2	4	-6	5.7	5.8
2	4	-5	8.9	-8.9
2	4	-4	15.9	-15.6
2	4	-3	3.4	-5.0
2	4	-2	9.1	7.0
2	4	-1	13.1	-11.7
2	4	0	9.6	9.9
2	4	1	3.2	2.7
2	4	2	3.0	-2.3
2	4	3	2.7	1.2
2	4	4	6.0	-5.3
2	4	5	7.6	8.5
2	4	6	18.7	19.6
2	4	7	14.1	14.0
2	4	8	33.8	-36.7
2	4	9	36.1	-38.2
2	4	10	19.5	19.0
2	4	11	6.8	-8.4
2	4	12	10.9	-10.3
2	4	13	7.6	8.0
2	4	14	15.1	-13.9
2	4	15	3.0	-2.2
2	4	16	16.2	-15.0
2	4	17	19.1	17.2
2	4	18	40.2	36.5
2	5	-18	9.2	-9.9
2	5	-17	12.7	-12.6
2	5	-16	18.7	20.5
2	5	-15	15.6	14.9
2	5	-14	7.4	7.1
2	5	-13	11.1	10.3
2	5	-12	2.5	1.5
2	5	-11	14.0	-13.8
2	5	-10	10.0	10.0
2	5	-9	24.6	-24.2
2	5	-8	6.8	6.3
2	5	-7	2.8	-1.8
2	5	-6	9.5	8.4
2	5	-5	23.5	23.0
2	5	-4	18.4	17.5
2	5	-3	18.5	18.8
2	5	-2	5.5	5.0
2	5	-1	1.9	-0.7
2	5	0	10.3	-11.7
2	5	1	12.4	-12.2
2	5	2	16.2	15.6
2	5	3	6.1	4.5
2	5	4	10.0	-8.5
2	5	5	10.5	-10.8
2	5	6	9.3	-6.9
2	5	7	3.6	-6.4
2	5	8	7.6	-4.8
2	5	9	11.6	-9.1
2	5	10	21.0	18.0
2	5	11	28.3	-26.1
2	5	12	23.9	-20.8
2	5	13	7.8	-8.4
2	5	14	48.2	50.6
2	5	15	19.3	-19.4
2	5	16	2.0	-0.1
2	5	17	18.2	-16.3
2	5	18	5.1	-5.6
2	6	-18	9.0	8.7
2	6	-17	15.6	15.6
2	6	-16	6.7	-7.8
2	6	-15	3.3	3.5
2	6	-14	11.7	10.8
2	6	-13	6.7	4.9
2	6	-12	3.1	-2.7
2	6	-11	7.8	-7.7
2	6	-10	17.7	15.1
2	6	-9	2.4	1.7
2	6	-8	2.2	-2.1
2	6	-7	15.7	14.9
2	6	-6	16.8	17.3
2	6	-5	29.7	-28.8
2	6	-4	5.7	5.9
2	6	-3	24.7	25.7
2	6	-2	16.1	-15.9
2	6	-1	16.4	-15.3
2	6	0	3.2	-1.9
2	6	1	19.5	18.0
2	6	2	7.7	7.4
2	6	3	6.7	4.0
2	6	4	3.2	-1.0
2	6	5	11.4	-11.2
2	6	6	7.1	8.1
2	6	7	32.1	26.7
2	6	8	2.3	-1.5
2	6	9	4.7	-1.9
2	6	10	4.4	-4.5
2	6	11	14.2	-12.6
2	6	12	15.2	-13.0
2	6	13	16.5	18.2
2	6	14	2.8	-0.7
2	6	15	10.3	-9.2
2	6	16	30.0	31.1
2	6	17	26.7	24.7
2	6	18	6.8	7.1
2	7	-17	8.5	9.3
2	7	-16	15.2	14.6
2	7	-15	7.1	6.4
2	7	-14	19.5	-17.3
2	7	-13	7.9	6.7
2	7	-12	17.7	17.2
2	7	-11	6.1	-4.9
2	7	-10	11.3	-9.6
2	7	-9	25.4	-25.2
2	7	-8	6.9	-7.1
2	7	-7	2.9	-2.4
2	7	-6	9.6	9.2
2	7	-5	3.0	3.4
2	7	-4	8.5	9.3
2	7	-3	9.2	8.4
2	7	-2	2.9	-2.6
2	7	-1	23.1	-21.6
2	7	0	13.8	13.8
2	7	1	10.1	7.8
2	7	2	7.6	6.9
2	7	3	13.6	-15.3
2	7	4	20.3	19.0
2	7	5	2.8	-1.9
2	7	6	14.7	-14.6
2	7	7	28.9	29.4
2	7	8	17.1	-19.1
2	7	9	15.5	-14.1
2	7	10	6.8	6.0
2	7	11	3.3	-3.6
2	7	12	9.9	9.3
2	7	13	7.9	6.3
2	7	14	2.8	-2.8
2	7	15	20.8	20.4
2	7	16	5.3	4.4
2	7	17	33.8	-38.2
2	7	18	6.9	-6.1
2	8	-17	37.4	35.9
2	8	-16	18.3	19.0
2	8	-15	3.0	1.8
2	8	-14	33.2	-33.7
2	8	-13	11.7	12.0
2	8	-12	8.2	-9.1
2	8	-11	8.5	-7.2
2	8	-10	3.1	3.0
2	8	-9	16.7	15.8
2	8	-8	2.8	-3.3
2	8	-7	12.3	-11.8
2	8	-6	11.4	11.7
2	8	-5	12.9	13.1
2	8	-4	6.0	4.8
2	8	-3	2.9	-1.9
2	8	-2	3.1	4.9
2	8	-1	10.6	-10.4
2	8	0	24.5	-21.7
2	8	1	7.1	7.4
2	8	2	8.2	-9.5
2	8	3	11.4	10.0
2	8	4	17.3	18.0
2	8	5	3.0	2.4
2	8	6	2.9	-1.1
2	8	7	6.1	-5.5
2	8	8	19.4	19.0
2	8	9	26.5	26.6
2	8	10	9.8	10.0
2	8	11	7.7	-7.0
2	8	12	3.7	1.8
2	8	13	7.6	6.9
2	8	14	3.4	3.3
2	8	15	10.4	-10.0
2	8	16	6.2	6.6
2	8	17	3.2	-0.6
2	8	18	3.1	1.9
2	9	-17	11.0	11.1
2	9	-16	2.9	4.5
2	9	-15	11.6	-12.1
2	9	-14	11.2	-11.7
2	9	-13	3.0	-1.0
2	9	-12	3.1	-1.8
2	9	-11	8.3	-8.0
2	9	-10	8.5	-8.7
2	9	-9	13.2	-13.2
2	9	-8	10.4	-9.8
2	9	-7	9.4	-9.8
2	9	-6	14.4	-15.0
2	9	-5	7.7	8.1
2	9	-4	6.6	7.6
2	9	-3	18.8	-19.6
2	9	-2	13.2	-13.2
2	9	-1	15.4	17.4
2	9	0	3.2	6.1
2	9	1	15.5	-16.3
2	9	2	4.5	4.7
2	9	3	4.4	-4.5
2	9	4	12.6	11.4
2	9	5	15.2	-13.0
2	9	6	16.5	16.2
2	9	7	2.8	-0.7
2	9	8	10.3	-10.1
2	9	9	31.0	31.1
2	9	10	26.7	24.7
2	9	11	7.1	6.4
2	9	12	19.5	-17.3
2	9	13	7.9	6.7
2	9	14	17.7	17.2
2	9	15	6.1	-4.9
2	9	16	11.3	-9.6
2	9	17	25.4	-25.2
2	9	18	6.9	-7.1
2	10	-17	2.9	-2.4
2	10	-16	9.6	9.2
2	10	-15	3.0	3.4
2	10	-14	8.5	9.3
2	10	-13	9.2	8.4
2	10	-12	2.9	-2.6
2	10	-11	23.1	-21.6
2	10	-10	13.8	13.8
2	10	-9	10.1	7.8
2	10	-8	7.6	6.9
2	10	-7	13.6	-15.3
2	10	-6	20.3	19.0
2	10	-5	2.8	-1.9
2	10	-4	14.7	-14.6
2	10	-3	28.9	29.4
2	10	-2	17.1	-19.1
2	10	-1	15.5	-14.1
2	10	0	6.8	6.0
2	10	1	3.3	-3.6
2	10	2	9.9	9.3
2	10	3	7.9	6.3
2	10	4	2.8	-2.8
2	10	5	20.8	20.4
2	10	6	5.3	4.4
2	10	7	33.8	-38.2
2	10	8	6.9	-6.1
2	10	9	37.4	35.9
2	10	10	18.3	19.0
2	10	11	3.0	1.8
2	10	12	33.2	-33.7
2	10	13	11.7	12.0
2	10	14	8.2	-9.1
2	10	15	8.5	-7.2
2	10	16	3.1	3.0
2	10	17	16.7	15.8
2	10	18	2.8	-3.3
2	11	-17	12.3	-11.8
2	11	-16	11.4	11.7
2	11	-15	12.9	13.1
2	11	-14	6.0	4.8
2	11	-13	2.9	-1.9
2	11	-12	3.1	4.9
2	11	-11	10.6	-10.4
2	11	-10	24.5	-21.7
2	11	-9	7.1	7.4
2	11	-8	8.2	-9.5
2	11	-7	11.4	10.0
2	11	-6	17.3	18.0
2	11	-5	3.0	2.4
2	11	-4	2.9	-1.1
2	11	-3	6.1	-5.5
2	11	-2	19.4	19.0
2	11	-1	26.5	26.6
2	11	0	9.8	10.0
2	11	1	7.7	-7.0
2	11	2	3.7	1.8
2	11	3	7.6	6.9
2	11	4	3.4	3.3
2	11	5	10.4	-10.0
2	11	6	6.2	6.6
2	11	7	3.2	-0.6
2	11	8	3.1	1.9
2	11	9	11.0	11.1
2	11	10	2.9	4.5
2	11	11	11.6	-12.1
2	11	12	11.2	-11.7
2	11	13	3.0	-1.0
2	11	14	3.1	-1.8
2	11	15	8.3	-8.0
2	11	16	8.5	-8.7
2	11	17	13.2	-13.2
2	11	18	10.4	-9.8
2	12	-17	9.4	-9.8
2	12	-16	14.4	-15.0
2	12	-15	7.7	8.1
2	12	-14	6.6	7.6
2	12	-13	18.8	-19.6
2	12	-12	13.2	-13.2
2	12	-11	15.4	17.4
2	12	-10	3.2	6.1
2	12	-9	15.5	-16.3
2	12	-8	4.5	4.7
2	12	-7	4.4	-4.5
2	12	-6	12.6	11.4
2	12	-5	15.2	-13.0
2	12	-4	16.5	16.2
2	12	-3	2.8	-0.7
2	12	-2	10.3	-10.1
2	12	-1	31.0	31.1
2	12	0	26.7	24.7
2	12	1	7.1	6.4
2	12	2	19.5	-17.3
2	12	3	7.9	6.7
2	12	4	17.7	17.2
2	12	5	6.1	-4.9
2	12	6	11.3	-9.6
2	12	7	25.4	-25.2
2	12	8	6.9	-7.1
2	12	9	2.9	-2.4
2	12	10	9.6	9.2
2	12	11	3.0	3.4
2	12	12	8.5	9.3
2	12	13	9.2	8.4
2	12	14	2.9	-2.6
2	12	15	23.1	-21.6
2	12	16	13.8	13.8
2	12	17	10.1	7.8
2	12	18	7.6	6.9
2	13	-17	13.6	-15.3
2	13	-16	20.3	19.0
2	13	-15	2.8	-1.9
2	13	-14	14.7	-14.6
2	13	-13	28.9	29.4
2	13	-12	17.1	-19.1
2	13	-11	15.5	-14.1
2	13	-10	6.8	6.0
2	13	-9	3.3	-3.6
2	13	-8	9.9	9.3
2	13	-7	7.9	6.3
2	13	-6	2.8	-2.8
2	13	-5	20.8	20.4
2	13	-4	5.3	4.4
2	13	-3	33.8	-38.2
2	13	-2	6.9	-6.1
2	13	-1	37.4	35.9
2	13	0	18.3	19.0
2	13	1	3.0	1.8
2	13	2	33.2	-33.7
2	13	3	11.7	12.0
2	13	4	8.2	-9.1
2	13	5	8.5	-7.2
2	13	6	3.1	3.0
2	13	7	16.7	15.8
2	13	8	2.8	-3.3
2	14	-17	12.3	-11.8
2	14	-16	11.4	11.7
2	14	-15	12.9	13.1
2	14	-14	6.0	4.8
2	14	-13	2.9	-1.9
2	14	-12	3.1	4.9
2	14	-11	10.6	-10.4
2	14	-10	24.5	-21.7
2	14	-9	7.1	7.4
2	14	-8	8.2	-9.5
2	14	-7	11.4	10.0
2	14	-6	17.3	18.0
2	14	-5	3.0	2.4
2	14	-4	2.9	-1.1
2	14	-3	6.1	-5.5
2	14	-2	19.4	19.0
2	14	-1	26.5	26.6
2	14	0	9.8	10.0
2	14	1	7.7	-7.0
2	14	2	3.7	1.8
2	14	3	7.6	6.9
2	14	4	3.4	3.3
2	14	5	10.4	-10.0
2	14	6	6.2	6.6
2	14	7	3.2	-0.6
2	14	8	3.1	1.9
2	14	9	11.0	11.1
2	14	10	2.9	4.5
2	14	11	11.6	-12.1
2	14	12	11.2	-11.7
2	14	13	3.0	-1.0
2	14	14	3.1	-1.8
2	14	15	8.3	-8.0
2	14	16	8.5	-8.7
2	14	17	13.2	-13.2
2	14	18	10.4	-9.8
2	15	-17	9.4	-9.8
2	15	-16	14.4	-15.0
2	15	-15	7.7	8.1
2	15	-14	6.6	7.6
2	15	-13	18.8	-19.6
2	15	-12	13.2	-13.2
2	15	-11	15.4	17.4
2	15	-10	3.2	6.1
2	15	-9	15.5	-16.3
2	15	-8	4.5	4.7
2	15	-7	4.4	-4.5
2	15	-6	12.6	11.4
2	15	-5	15.2	-13.0
2	15	-4	16.5	16.2
2	15	-3	2.8	-0.7
2	15	-2	10.3	-10.1
2	15	-1	31.0	31.1
2	15	0	26.7	24.7
2	15	1	7.1	6.4
2	15	2	19.5	-17.3
2	15	3	7.9	6.7
2	15	4	17.7	17.2
2	15	5	6.1	-4.9
2	15	6	11.3	-9.6
2	15	7	25.4	-25.2
2	15	8	6.9	-7.1
2	15	9	2.9	-2.4
2	15	10	9.6	9.2
2	15	11	3.0	3.4
2	15	12	8.5	9.3
2	15	13	9.2	8.4
2	15	14	2.9	-2.6
2	15	15	23.1	-21.6
2	15	16	13.8	13.8
2	15	17	10.1	7.8
2	15	18	7.6	6.9
2	16	-17	13.6	-15.3
2	16	-16	20.3	19.0
2	16	-15	2.8	-1.9
2	16	-14	14.7	-14.6
2	16	-13	28.9	29.4
2	16	-12	17.1	-19.1
2	16	-11	15.5	-14.1
2	16	-10	6.8	6.0
2	16	-9	3.3	-3.6
2	16	-8	9.9	9.3
2	16	-7	7.9	6.3
2	16	-6	2.8	-2.8
2	16	-5	20.8	20.4
2	16	-4	5.3	4.4
2	16	-3	33.8	-38.2
2	16	-2	6.9	-6.1
2	16	-1	37.4	35.9
2	16	0	18.3	19.0
2	16	1	3.0	1.8
2	16	2	33.2	-33.7
2	16	3	11.7	12.0
2	16	4	8.2	-9.1
2	16	5	8.5	-7.2
2	16	6	3.1	3.0
2	16	7	16.7	15.8
2	16	8	2.8	-3.3
2	17	-17	12.3	-11.8
2	17	-16	11.4	11.7
2	17	-15	12.9	13.1
2	17	-14	6.0	4.8
2	17	-13	2.9	-1.9
2	17	-12	3.1	4.9
2	17	-11	10.6	-10.4
2	17	-10	24.5	-21.7
2	17	-9	7.1	7.4
2	17	-8	8.2	-9.5
2	17	-7	11.4	10.0
2	17	-6	17.3	18.0
2	17	-5	3.0	2.4
2	17	-4	2.9	-1.1
2	17	-3	6.1	-5.5
2	17	-2	19.4	19.0
2	17	-1	26.5	26.6
2	17	0	9.8	10.0
2	17	1	7.7	-7.0
2	17	2	3.7	1.8
2	17	3	7.6	6.9
2	17	4	3.4	3.3
2	17	5	10.4	-10.0
2	17	6	6.2	6.6
2	17	7	3.2	-0.6
2	17	8	3.1	1.9
2	17	9	11.0	11.1
2	17	10	2.9	4.5
2	17	11	11.6	-12.1
2	17	12	11.2	-11.7
2	17	13	3.0	-1.0
2	17	14	3.1	-1.8
2	17	15	8.3	-8.0
2	17	16	8.5	-8.7
2	17	17	13.2	-13.2
2	17	18	10.4	-9.8
2	18	-17	9.4	-9.8
2	18	-16	14.4	-15.0
2	18	-15	7.7	8.1
2	18	-14	6.6	7.6
2	18	-13	18.8	-19.6
2	18	-12	13.2	-13.2
2	18	-11	15.4	17.4
2	18	-10	3.2	6.1
2	18	-9	15.5	-16.3
2	18	-8	4.5	4.7
2	18	-7	4.4	-4.5
2	18	-6	12.6	11.4
2	18	-5	15.2	-13.0
2	18	-4	16.5	16.2
2	18	-3	2.8	-0.7
2	18	-2	10.3	-10.1
2	18	-1	31.0	31.1
2	18	0	26.7	24.7
2	18	1	7.1	6.4
2	18	2	19.5	-17.3
2	18	3	7.9	6.7
2	18	4	17.7	17.2
2	18	5	6.1	-4.9
2	18	6	11.3	-9.6
2	18	7	25.4	-25.2
2	18	8	6.9	-7.1
2	18	9	2.9	-2.4
2	18	10	9.6	9.2
2	18	11	3.0	3.4
2	18	12	8.5	9.3
2	18	13	9.2	8.4
2	18	14	2.9	-2.6
2	18	15	23.1	-21.6
2	18	16	13.8	13.8
2	18	17	10.1	7.8
2	18	18	7.6	6.9
2	19	-17	13.6	-15.3
2	19	-16	20.3	19.0
2	19	-15	2.8	-1.9
2	19	-14	14.7	-14.6
2	19	-13	28.9	29.4
2	19	-12	17.1	-19.1
2	19	-11	15.5	-14.1
2	19	-10	6.8	6.0
2	19	-9	3.3	-3.6
2	19	-8	9.9	9.3
2	19	-7	7.9	6.3
2	19	-6	2.8	-2.8
2	19	-5	20.8	20.4
2	19	-4	5.3	4.4
2	19	-3	33.8	-38.2
2	19	-2	6.9	-6.1
2	19	-1	37.4	35.9
2	19	0	18.3	19.0
2	19	1	3.0	1.8
2	19	2	33.2	-33.7
2	19	3	11.7	12.0
2	19	4	8.2	-9.1
2	19	5	8.5	-7.2
2	19	6	3.1	3.0
2	19	7	16.7	15.8
2	19	8	2.8	-3.3
2	20	-17	12.3	-11.8
2	20	-16	11.4	11.7
2	20	-15	12.9	13.1
2	20	-14	6.0	4.8
2	20	-13	2.9	-1.9
2	20	-12	3.1	4.9
2	20	-11	10.6	-10.4
2	20	-10	24.5	-21.7
2	20	-9	7.1	7.4
2	20	-8	8.2	-9.5
2	20	-7	11.4	10.0
2	20	-6	17.3	18.0
2	20	-5	3.0	2.4
2	20	-4	2.9	-1.1
2	20	-3	6.1	-5.5
2	20	-2	19.4	19.0
2	20	-1	26.5	26.6
2	20	0	9.8	10.0
2	20	1	7.7	-7.0
2	20	2	3.7	1.8
2	20	3	7.6	6.9
2	20	4	3.4	3.3
2	20	5	10.4	-10.0
2	20	6	6.2	6.6
2	20	7	3.2	-0.6
2	20	8	3.1	1.9
2	20	9	11.0	11.1
2	20	10	2.9	4.5
2	20	11	11.6	-12.1
2	20	12	11.2	-11.7
2	20	13	3.0	-1.0
2	20	14	3.1	-1.8
2	20	15	8.3	-8.0
2	20	16	8.5	-8.7
2	20	17	13.2	-13.2
2	20	18	10.4	-9.8
2	21	-17	9.4	-9.8
2	21	-16	14.4	-15.0
2	21	-15	7.7	8.1
2	21	-14	6.6	7.6
2	21	-13	18.8	-19.6
2	21	-12	13.2	-13.2
2	21	-11	15.4	17.4
2	21	-10	3.2	6.1
2	21	-9	15.5	-16.3
2	21	-8	4.5	4.7
2	21	-7	4.4	-4.5
2	21	-6	12.6	11.4
2	21	-5	15.2	-13.0
2	21	-4	16.5	16.2
2	21	-3	2.8	-0.7
2	21	-2	10.3	-10.1
2	21	-1	31.0	31.1
2	21	0	26.7	24.7
2	21	1	7.1	6.4
2	21	2	19.5	-17.3
2	21	3	7.9	6.7
2	21	4	17.7	17.2
2	21	5	6.1	-4.9
2	21	6	11.3	-9.6
2	21	7	25.4	-25.2
2	21	8	6.9	-7.1
2	21	9	2.9	-2.4
2	21	10	9.6	9.2
2

TABLE 4.4

FRACTIONAL COORDINATES AND E.S.D.S.

Atom	x/a	y/b	z/c
Cl	-0.3367 ± 5	0.2575 ± 1	0.1991 ± 2
O(1)	0.1558 ± 12	0.1934 ± 2	0.3219 ± 5
O(2)	0.0993 ± 14	0.0316 ± 2	0.2449 ± 5
C(1)	-0.2743 ± 15	0.1677 ± 2	0.1581 ± 6
C(2)	-0.4036 ± 16	0.2090 ± 2	0.1108 ± 7
C(3)	-0.5972 ± 16	0.2154 ± 3	-0.0060 ± 7
C(4)	-0.6555 ± 17	0.1785 ± 3	-0.0823 ± 7
C(5)	-0.5712 ± 18	0.1000 ± 3	-0.1301 ± 7
C(6)	-0.4390 ± 19	0.0576 ± 3	-0.0991 ± 7
C(7)	-0.2662 ± 19	0.0507 ± 2	0.0190 ± 8
C(8)	-0.2142 ± 15	0.0837 ± 2	0.1106 ± 6
C(9)	-0.3391 ± 14	0.1289 ± 2	0.0794 ± 6
C(10)	-0.5241 ± 15	0.1351 ± 2	-0.0419 ± 6
C(11)	-0.1459 ± 15	0.0856 ± 2	0.3491 ± 6
C(12)	-0.2018 ± 18	0.0556 ± 3	0.4416 ± 7
C(13)	-0.2623 ± 20	0.0725 ± 3	0.5503 ± 8
C(14)	-0.2576 ± 18	0.1178 ± 3	0.5740 ± 7
C(15)	-0.1896 ± 16	0.1469 ± 3	0.4849 ± 7
C(16)	-0.1419 ± 16	0.1304 ± 2	0.3717 ± 6
C(17)	-0.0644 ± 14	0.1651 ± 2	0.2853 ± 6
C(18)	-0.0641 ± 15	0.0666 ± 2	0.2362 ± 7

TABLE 4.5

ORTHOGONALISED COORDINATES AND E.S.D.S.(in Å)
REFERRED TO THE AXES PARALLEL TO a*, b and c.

ATOM	X	Y	Z
Cl	-1.310 ± 2	7.680 ± 2	2.482 ± 2
O(1)	0.606 ± 5	5.768 ± 5	3.455 ± 6
O(2)	0.386 ± 5	0.944 ± 5	2.644 ± 6
C(1)	-1.068 ± 6	5.004 ± 6	1.977 ± 7
C(2)	-1.571 ± 6	6.233 ± 7	1.554 ± 7
C(3)	-2.324 ± 6	6.425 ± 7	0.410 ± 8
C(4)	-2.551 ± 7	5.325 ± 8	-0.392 ± 8
C(5)	-2.223 ± 7	2.982 ± 8	-0.991 ± 8
C(6)	-1.709 ± 7	1.717 ± 8	-0.752 ± 8
C(7)	-1.036 ± 7	1.513 ± 7	0.423 ± 9
C(8)	-0.834 ± 6	2.496 ± 6	1.401 ± 7
C(9)	-1.320 ± 5	3.845 ± 6	1.154 ± 7
C(10)	-2.040 ± 6	4.029 ± 7	-0.047 ± 7
C(11)	-0.568 ± 6	2.553 ± 6	3.998 ± 7
C(12)	-0.785 ± 7	1.657 ± 8	5.072 ± 8
C(13)	-1.021 ± 8	2.162 ± 8	6.328 ± 9
C(14)	-1.002 ± 7	3.513 ± 9	6.589 ± 8
C(15)	-0.738 ± 6	4.381 ± 8	5.543 ± 8
C(16)	-0.552 ± 6	3.890 ± 6	4.246 ± 7
C(17)	-0.250 ± 6	4.925 ± 6	3.224 ± 7
C(18)	-0.250 ± 6	1.986 ± 6	2.678 ± 8

TABLE 4.6

ASSUMED FRACTIONAL CO-ORDINATES OF THE HYDROGEN ATOMS AND ISOTROPIC TEMPERATURE FACTORS

Atom	x/a	y/b	z/c	Uiso
H(3)	-0.650	0.248	-0.056	0.06
H(4)	-0.830	0.184	-0.177	0.06
H(5)	-0.766	0.112	-0.218	0.07
H(6)	-0.535	0.029	-0.182	0.07
H(7)	-0.175	0.024	0.037	0.06
H(12)	-0.203	0.023	0.422	0.06
H(13)	-0.325	0.045	0.628	0.07
H(14)	-0.308	0.135	0.658	0.07
H(15)	-0.150	0.182	0.499	0.06

TABLE 4.7

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.
$o2$
(in A)

ATOM	U11	U22	U33	2U23	2U31	2U12
Cl	0.0727 13	0.0455 10	0.0939 18	0.0061 21	0.0340 22	0.0012 16
O(1)	0.0523 29	0.0610 30	0.0872 41	-0.0225 56	-0.0074 50	-0.0242 43
O(2)	0.0806 36	0.0536 30	0.0969 46	-0.0083 58	-0.0166 60	0.0376 49
C(1)	0.0383 36	0.0408 35	0.0586 49	0.0004 66	0.0143 59	-0.0044 49
C(2)	0.0423 39	0.0573 41	0.0642 53	0.0195 75	0.0269 65	0.0073 57
C(3)	0.0388 40	0.0797 51	0.0779 60	0.0442 89	0.0101 71	0.0029 65
C(4)	0.0481 42	0.0818 51	0.0628 55	0.0408 86	0.0018 68	0.0174 69
C(5)	0.0526 45	0.0982 59	0.0581 56	0.0013 91	0.0240 72	-0.0210 77
C(6)	0.0567 47	0.0930 57	0.0645 58	-0.0356 94	0.0160 75	-0.0261 76
C(7)	0.0613 46	0.0629 45	0.0752 59	-0.0060 85	0.0352 76	-0.0098 67
C(8)	0.0345 35	0.0533 38	0.0574 48	0.0109 69	0.0134 57	-0.0044 52

P . T . O .

TABLE 4.7 cont.

ATOM	U11	U22	U33	2U23	2U31	2U12
C(9)	0.0283 33	0.0597 39	0.0421 44	0.0290 66	0.0018 53	-0.0049 51
C(10)	0.0356 38	0.0727 46	0.0574 53	-0.0152 77	0.0304 64	-0.0102 59
C(11)	0.0340 35	0.0556 39	0.0509 47	-0.0076 69	-0.0059 56	-0.0093 53
C(12)	0.0545 46	0.0847 55	0.0588 57	0.0228 88	-0.0129 72	0.0081 74
C(13)	0.0643 51	0.0840 57	0.0830 69	0.0666 99	-0.0158 85	-0.0059 79
C(14)	0.0426 43	0.1134 65	0.0625 58	0.0008 96	-0.0115 70	-0.0057 77
C(15)	0.0357 39	0.0893 53	0.0667 57	0.0402 88	-0.0038 65	0.0053 66
C(16)	0.0438 37	0.0514 38	0.0464 48	0.0072 68	0.0087 58	0.0024 54
C(17)	0.0280 34	0.0540 39	0.0700 52	-0.0181 71	0.0166 58	0.0092 51
C(18)	0.0326 36	0.0472 38	0.0914 61	-0.0066 78	-0.0315 66	0.0018 54

TABLE 4.8

PRINCIPAL VALUES OF THE VIBRATION TENSORS AND THEIR DIRECTION COSINES REFERRED TO THE ORTHOGONAL AXES PARALLEL TO a*, b and c

ATOM	U / Å^2	D1	D2	D3
Cl	0.0453	0.0164	-0.9980	0.0607
	0.0943	0.1141	0.0622	0.9915
	0.0724	-0.9933	-0.0094	0.1149
O(1)	0.0386	0.7878	0.5427	0.2912
	0.0998	-0.2556	-0.1420	0.9563
	0.0695	0.5603	-0.8278	0.0268
O(2)	0.1266	-0.5355	-0.2281	0.8132
	0.0436	0.4960	-0.8642	0.0842
	0.0719	0.6836	0.4484	0.5759
C(1)	0.0597	-0.0298	0.0381	0.9988
	0.0370	0.8648	0.5020	0.0067
	0.0420	-0.5012	0.8640	-0.0479
C(2)	0.0712	0.2111	0.5786	0.7878
	0.0410	-0.9774	0.1206	0.1734
	0.0505	0.0053	-0.8066	0.5911
C(3)	0.1025	-0.0156	0.6983	0.7156
	0.0383	0.9884	-0.0973	0.1165
	0.0584	0.1510	0.7091	-0.6887
C(4)	0.0950	0.0490	0.8320	0.5526
	0.0384	0.7862	-0.3733	0.4924
	0.0637	0.6160	0.4104	-0.6724
C(5)	0.1006	-0.2115	0.9757	0.0568
	0.0498	-0.9430	-0.2190	0.2507
	0.0581	0.2571	-0.0006	0.9664
C(6)	0.1026	0.2295	-0.9029	0.3634
	0.0480	0.7826	0.3932	0.4826
	0.0654	-0.5786	0.1737	0.7969

P . T . O .

TABLE 4.8 cont.

ATOM	U A o2	D1	D2	D3
C(7)	0.0766	0.3954	-0.2723	0.8772
	0.0566	-0.8039	-0.5645	0.1871
	0.0645	0.4442	-0.7792	-0.4421
C(8)	0.0342	-0.9924	-0.1210	0.0204
	0.0625	-0.0506	0.5551	0.8302
	0.0495	-0.1117	0.8229	-0.5571
C(9)	0.0698	-0.1124	0.8383	0.5334
	0.0268	0.9411	-0.0825	0.3279
	0.0361	0.3189	0.5389	-0.7797
C(10)	0.0324	-0.9436	-0.0654	0.3246
	0.0764	0.1866	-0.9148	0.3582
	0.0545	0.2736	0.3986	0.8754
C(11)	0.0290	0.9105	0.1991	0.3624
	0.0599	-0.2968	-0.2954	0.9081
	0.0564	0.2878	-0.9344	-0.2099
C(12)	0.0396	0.7715	-0.2128	0.5996
	0.0903	-0.1495	0.8554	0.4959
	0.0756	-0.6185	-0.4722	0.6281
C(13)	0.1283	-0.2764	0.6033	0.7481
	0.0445	0.5957	-0.5033	0.6260
	0.0681	0.7541	0.6187	-0.2203
C(14)	0.0361	0.9154	0.0286	0.4016
	0.1136	-0.0479	0.9981	0.0382
	0.0757	-0.3997	-0.0542	0.9150
C(15)	0.1025	-0.0439	0.8311	0.5544
	0.0324	0.9435	-0.1480	0.2966
	0.0619	0.3285	0.5360	-0.7776
C(16)	0.0403	0.7938	-0.2553	0.5520
	0.0539	-0.1902	0.7579	0.6240
	0.0494	-0.5777	-0.6003	0.5531
C(17)	0.0755	0.0107	-0.4264	0.9045
	0.0267	-0.9729	0.2044	0.1079
	0.0504	-0.2309	-0.8811	-0.4127
C(18)	0.1101	-0.2819	-0.0581	0.9577
	0.0259	0.9592	0.0066	0.2827
	0.0470	-0.0228	0.9983	0.0539

TABLE 4.9

Displacements (in Å) of atoms from mean planes through

a) all atoms

b) atoms of naphthalene ring system

c) atoms of naphthalene ring adjacent to Cl atom

d) atoms of naphthalene ring remote from Cl atom

e) atoms of phthaloyl ring

f) atoms C(1) , C(8) , C(11) and C (16)

Atom	(a)	(b)	(c)	(d)	(e)	(f)
Cl	0.150	0.160	0.034	0.396	1.258	-0.073
O(1)	1.601	0.911	-	-	-0.893	1.494
O(2)	1.058	0.056	-	-	-0.761	0.909
C(1)	0.215	0.023	-0.001	-	0.983	-0.030
C(2)	-0.054	0.065	0.014	-	1.613	-0.346
C(3)	-0.518	0.010	-0.012	-	2.571	-
C(4)	-0.680	-0.041	-0.003	-	2.887	-
C(5)	-0.477	0.012	-	-0.005	2.561	-
C(6)	-0.161	0.060	-	0.008	1.951	-
C(7)	0.217	0.028	-	0.003	1.067	-0.134
C(8)	0.304	-0.052	-	-0.017	0.738	0.030

P . T . O .

TABLE 4.9 Cont.

Atom	(a)	(b)	(c)	(d)	(e)	(f)
C(9)	0.027	-0.052	-0.014	0.020	1.325	-
C(10)	-0.394	-0.053	0.016	-0.009	2.260	-0.810
C(11)	0.008	-1.050	-	-	0.007	-0.057
C(12)	-0.529	-1.943	-	-	-0.017	-0.507
C(13)	-0.976	-2.632	-	-	0.010	-
C(14)	-0.874	-2.446	-	-	0.009	-
C(15)	-0.300	-1.532	-	-	-0.019	-0.253
C(16)	0.109	-0.864	-	-	0.011	0.058
C(17)	0.731	0.107	0.047	0.274	-0.050	0.597
C(18)	0.543	-0.274	-0.220	-0.220	-0.093	0.381

TABLE 4.10

SOME SHORT INTERATOMIC DISTANCES (in Å)

Intramolecular distances(<3.5Å)

Atom A	Atom B	A-B	Atom A	Atom B	A-B
Cl	C(3)	2.626	C(3)	C(9)	2.867
Cl	C(1)	2.734	C(4)	C(5)	2.441
Cl	O(1)	2.877	C(4)	C(9)	2.469
Cl	C(17)	3.044	C(5)	C(7)	2.360
C(1)	O(1)	2.361	C(5)	C(9)	2.483
C(1)	C(10)	2.448	C(5)	C(8)	2.809
C(1)	C(3)	2.461	C(6)	C(10)	2.440
C(1)	C(16)	2.580	C(6)	C(8)	2.451
C(1)	C(8)	2.584	C(6)	C(9)	2.883
C(1)	C(4)	2.813	C(7)	C(18)	2.434
C(1)	C(18)	3.204	C(7)	C(9)	2.461
C(1)	C(11)	3.216	C(7)	O(2)	2.698
C(2)	C(4)	2.360	C(7)	C(10)	2.750
C(2)	C(9)	2.434	C(8)	O(2)	2.333
C(2)	C(17)	2.499	C(8)	C(10)	2.430
C(2)	C(10)	2.764	C(8)	C(11)	2.611
C(2)	O(1)	2.978	C(8)	C(17)	3.093
C(3)	C(10)	2.456	C(9)	C(17)	2.568

P . T . O .

TABLE 4.10 cont.

Atom A	Atom B	A-B	Atom A	Atom B	A-B
C(9)	C(18)	2.632	C(12)	O(2)	2.789
C(9)	C(16)	3.187	C(13)	C(15)	2.371
C(9)	C(11)	3.213	C(13)	C(16)	2.746
C(11)	C(15)	2.400	C(14)	C(16)	2.415
C(11)	C(13)	2.406	C(15)	C(17)	2.432
C(11)	O(1)	3.465	C(15)	O(1)	2.845
C(12)	C(16)	2.392	C(16)	O(1)	2.344
C(12)	C(14)	2.407	C(16)	C(18)	2.486
C(12)	C(18)	2.475	C(16)	O(2)	3.483
C(12)	C(15)	2.765	C(17)	C(18)	2.989

Intermolecular distances (<3.78Å)

Atom A	Atom B	E.P.*	Cell**	A-B
Cl	O(1)	1	-1 0 0	3.270
Cl	C(4)	2	0 0 0	3.522
Cl	C(3)	2	0 0 0	3.721
C(1)	O(1)	1	-1 0 0	3.269
C(1)	C(17)	1	-1 0 0	3.694
C(2)	O(1)	1	-1 0 0	3.232
C(2)	C(3)	1	1 0 0	3.696
C(3)	O(1)	2	-1 0 -1	3.359

P . T . O .

TABLE 4.10 cont.

Atom A	Atom B	E.P.*	Cell**	A-B
C(6)	O(2)	3	0 0 0	3.523
C(6)	C(7)	3	-1 0 0	3.608
C(7)	C(7)	3	-1 0 0	3.531
C(8)	O(2)	1	-1 0 0	3.703
C(11)	O(2)	1	-1 0 0	3.396
C(11)	C(18)	1	-1 0 0	3.656
C(12)	O(2)	1	-1 0 0	3.250
C(12)	C(13)	1	1 0 0	3.720
C(12)	C(18)	1	-1 0 0	3.731
C(14)	C(15)	1	-1 0 0	3.738
C(15)	O(1)	1	-1 0 0	3.175
C(16)	O(1)	1	-1 0 0	3.316
C(16)	C(17)	1	-1 0 0	3.743
C(17)	O(1)	1	-1 0 0	3.314
C(18)	O(2)	1	-1 0 0	3.503

* Integers under this column refer to the following equivalent positions

1) x , y , z ;
2) x , 1/2 - y , 1/2 + z ;
3) - x , - y , - z ;

** For any distance the triple set of integers given under this column indicate the unit-cell translation that must be added to the appropriate equivalent position to derive the co-ordinates of the atom under the column Atom B from those given in Table 4.4 .

2.4.7 Discussion

The molecule of 2-chloro-1, 8-phthaloylnaphthalene is not planar but is folded about a line through the two carbonyl carbon atoms, C(17) and C(18). This is not unexpected in view of the valency angles subtended by the atoms forming the 7-membered ring. The presence of the bulky Cl atom has caused further deformation and consequently a simple folded model does not adequately describe the molecule. Twist accompanied by folding has caused the non-symmetrical distortion of the molecule, a view of which can be seen in Fig. 4.5.

The equation of the mean plane through all the atoms of the molecule, calculated in the method of Schomaker et al. (1959), is

$$0.9708\ X' + 0.1045\ Y - 0.2160\ Z' + 1.1558 = 0 \qquad (3)$$

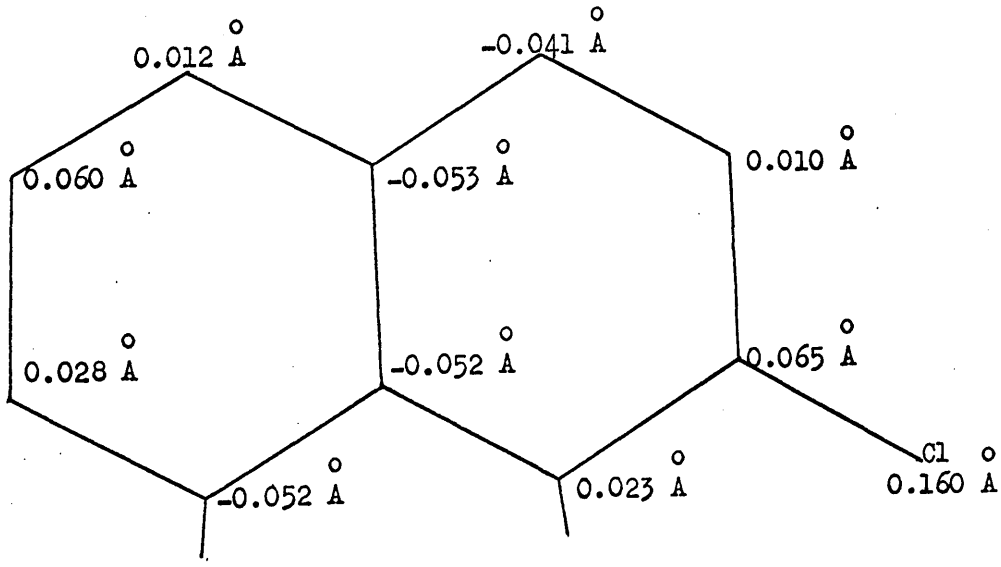
where X', Y and Z' (in Å) are the orthogonal co-ordinates with reference to axes parallel to a*, b and c. Root mean square displacement of the atoms from the mean plane is 0.616 Å. The appropriate χ^2 test (See Sec. I, 1.8.5) shows the significant non-planarity of the molecule which is further evident from an

examination of the deviations of the individual atoms from the mean plane [Table 4.9 (a)].

The best plane through the atoms, C(1) to C(10), of the naphthalene ring system has the equation

$$0.8515\ X' + 0.2184\ Y - 0.4767\ Z' + 0.7814 = 0 \qquad (4)$$

Root mean square distance of the atoms from this mean plane is 0.044 Å; the corresponding χ^2 test shows that the naphthalene ring system is not planar. Displacements of the various atoms out of this mean plane can be seen in Table 4.9 (b)



and the deviations of the naphthalene atoms are shown in the diagram which clearly indicates the buckling character of the naphthalene system.

The equation of the mean plane through the atoms of the six-membered ring of the naphthalene system, adjacent to the halogen atom, is

$$0.8444\ X' + 0.1847\ Y - 0.5029\ Z' + 0.9706 = 0 \qquad (5)$$

while that of the ring remote from the Cl atom is

$$0.8562\ X' + 0.2524\ Y - 0.4508\ Z' + 0.6992 = 0 \qquad (6)$$

The root mean square distance of the respective atoms out of the two planes are 0.011 and 0.012 $\mathring{A}$ respectively. The appropriate χ^2 tests show that both these rings of the naphthalene system are, to a good approximation, planar. Deviations of various atoms of the naphthalene system out of these two planes can be seen in Tables 4.9 (c) and 4.9 (d) respectively. The dihedral angle between these two mean planes is 4°. This non-planarity of the naphthalene ring system is, no doubt, due to the disturbance caused in the molecule by the halogen and phthaloyl substitutions.

The best fit of the plane through the atoms of the phthaloyl ring has the equation

$$-0.9822\,X' + 0.0480\,Y - 0.1819\,Z' + 0.0539 = 0 \qquad (7)$$

The root mean square deviation of the atoms of the ring from this plane is 0.013 Å. The appropriate χ^2 test indicates that the phthaloyl ring may be considered planar. Distances of some of the atoms of the molecule from this mean plane are given in Table 4.9 (e). The inter-planar angle between the mean planes through the naphthalene ring system (4) and the phthaloyl ring (7) is 42°. This may be compared with the similar dihedral angle (42°) in the case of phenoxthionine (Hosoya, 1966).

The incorporation of the parts of naphthalene and phthaloyl group in a seven-membered ring system has imposed strain in the molecule which is relieved mainly by bond angle deformation; but slight bond length extensions are also noticed in the affected peri-position of the naphthalene ring system. Thus valency bonds C(1) - C(9) and C(8) - C(9) have lengths 1.443 Å and 1.456 Å respectively while in normal naphthalene system these are both equal to 1.421 Å (Cruickshank and Sparks, 1960).

In absence of the halogen atom, one would have expected a symmetrical deformation of the seven-membered ring and hence of the molecule. The carbon atoms C(1) and C(8) of the naphthalene group and C(11) and C(16) of the phthaloyl system should be coplanar and the deviations of the atoms C(17) and O(1) from this plane should be equal to those of C(18) and O(2) respectively. In fact, the root mean square distance of the four atoms C(1), C(8), C(11) and C(16) from the mean plane through them, having equation

$$0.9857\,X' + 0.0993\,Y - 0.1364\,Z' + 0.7945 = 0 \qquad (8)$$

is 0.046 Å and the corresponding χ^2 test shows the significant non-planarity of these 4 atoms. The displacements of C(17) and O(1) from this plane are 0.597 and 1.494 Å while the corresponding deviations of C(18) and O(2) are 0.381 and 0.909 Å respectively [Table 4.9(f)]. This shows that the bulky halogen atom has caused the displacements of adjacent atoms C(17) and O(1) more than the remote atoms, C(18) and O(2), imposing a non-symmetrical distortion of the molecule.

Carbonyl carbon and oxygen atoms, C(17), O(1) and C(18), O(2) are displaced by 0.107, 0.911 and -0.274, 0.056 Å [Table 9.4 (b)] respectively from the naphthalene plane (4); the corresponding deviations from the mean plane through the phthaloyl ring (7) are -0.050, -0.893 and -0.093, -0.761 Å [Table 4.9 (e)] respectively. The effect of these increased displacements of the carbonyl group, adjacent to the halogen atom, is to increase the intramolecular separation of Cl...C(17) and Cl...O(1) to 3.044 and 2.877 Å (Fig. 4.6) which are still less than the normal van der Waals distances of 3.8 and 3.2 Å respectively.

Because of the strain imposed by the seven-membered ring and the halogen atom, the bonded distances of the naphthalene system are not comparable with those discussed by Cruickshank and Sparks (1960). The mean length of the bonds C(1) - C(9) and C(8) - C(9) is 1.450 Å (1.421 Å in naphthalene) and the average length of C(1) - C(2) and C(7) - C(8) is 1.397 Å (1.364 Å in naphthalene). Likewise, the valency angle C(8) - $\widehat{C(9)}$ - C(1) is increased from 121.75° (in naphthalene) to 126.2°. The other

angle displacements from the values found for naphthalene can likewise be explained in terms of the intramolecular overcrowding.

The average length of the four Csp^2 - Csp^2 bonds in the seven-membered ring is 1.4865 Å and is comparable with those of o-bromobenzoic acid, 1.487 Å (Ferguson and Sim, 1962 a) and benzoic acid, 1.48 Å (Sim, Robertson and Goodwin, 1955). Furthermore, it is similar to that of phthalic acid 1.495 Å (Nowaki and Jaggi, 1957, recalculated by Ferguson and Guy, 1966). Due to the intramolecular distortion complete agreement of the individual C-C bond lengths of the phthaloyl ring with those of the phthalic acid is not possible. However, the average of the C-C bond lengths (1.385 Å) in both the cases are the same.

The halogen atom does not cause any extension of the adjacent carbonyl bond; the C=O distances in the molecule are almost identical with a mean value of 1.223 Å. This also agrees well with that of o-chlorobenzoyl acetylene, 1.227 Å (see chapter 1) and is similar to the accepted value of 1.23 ± 0.01 Å (Int. Tables Vol. III, 1962). The aromatic C - Cl distance, 1.739 Å, is in

agreement with the values found in o-chlorobenzoyl acetylene (1.734 Å), o-chlorobenzoic acid (1.737 Å) and in 4-4'-dichloro-diphenyl sulphone (1.736 Å) [Sime and Abraham, 1960].

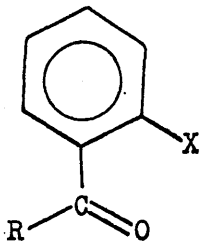
The intermolecular distances C(15)...O(1), 3.18, and C(2)...O(1), 3.23 Å appear to be slightly shorter than the normal van der Waals contact distance of 3.3 Å, but no hydrogen bond is possible here. No other intermolecular separation is shorter than the normal van der Waals distance (Table 4.10).

CHAPTER 5

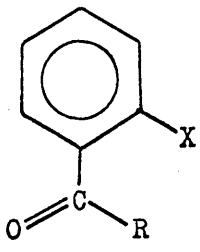
GENERAL DISCUSSION

2.5 INTRODUCTION

This discussion covers o-chlorobenzoylacetylene (I), o-bromobenzoylacetylene (II), o-fluorobenzoic acid (III), o-chlorobenzoic acid (IV), o-bromobenzoic acid (V), 2-chloro-5-nitrobenzoic acid (VI) and 2-chloro-1, 8-phthaloylnaphthalene (VII). Of these seven compounds, the structures of (IV), (V) and (VI) had already been reported (Ferguson and Sim, 1961, 1962 a and 1962 b), the others have been described in this thesis.



(A)



(B)

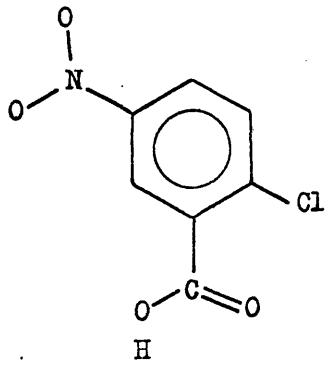
(I) X = Cl, R = -C≡CH

(II) X = Br, R = -C≡CH

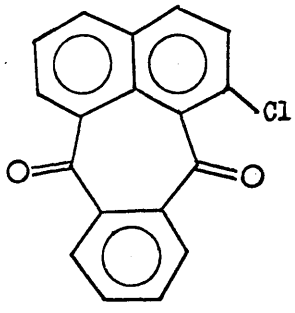
(III) X = F, R = -OH

(IV) X = Cl, R = -OH

(V) X = Br, R = -OH



(VI)



(VII)

2.5.1 Conformation

In all six o-halogeno-aroyl compounds (I - VI), the conformation adopted is (A), with the double bonded carbonyl (or carboxyl) oxygen adjacent to the halogen atom. A possible reason for this conformer being preferred to that of the type (B) in the crystal is that the $\rangle C{=}O$ grouping is less bulky than the $\geqslant C - R$ grouping, because,

a) the angle $C\text{-}\hat{C}{=}O$ is invariably greater than the angle $C\text{-}\hat{C}\text{-}R$,

b) the C=O bond length is shorter than C-R, which leads to an increased van der Waals separation of the carbonyl (or carboxyl) oxygen from the halogen atom over any other grouping for any given angle of rotation of C(arom.) - C(exocyclic) bond.

In the case of 2-chloro-1, 8-phthaloylnaphthalene, there is no possibility of the conformational isomerism of the type (A) or (B).

2.5.2 Intermolecular ethynyl hydrogen bond

The shift of the ethynyl hydrogen stretching frequency of benzoyl acetylene (Ph.CO.C:CH) from 3302 $cm.^{-1}$ in dilute carbon tetrachloride solution to 3225 $cm.^{-1}$ in the solid state has been attributed to intermolecular hydrogen bonding between ethynyl groups and the carbonyl oxygen atoms (Tyrrell, 1963). Both the o-halogenobenzoylacetylenes (I and II) show a similar spectral shift suggesting the presence of ethynyl hydrogen bonds in the structures. The x-ray crystal structure analysis has confirmed this prediction showing that both the compounds (I and II) are intermolecularly hydrogen bonded in the solid state.

The lengths and angles involved in the intermolecular ≡CH...O bonds in the o-halogenobenzoylacetylenes (I and II) are given in Table 5.1. This also contains the comparable figures for the similar hydrogen bond in propargyl 2-bromo-3-nitrobenzoate (Calabrese, McPhail and Sim, 1967). It shows that in all the cases $-C\equiv\hat{C}\ \ldots O$ (163°-168°), and hence presumably $\equiv\hat{C}-H\ldots O$. angles are less than 180° i.e. the intermolecular ethynyl hydrogen bonds in these compounds may be considered non-linear.

TABLE 5.1

DISTANCES AND ANGLES ASSOCIATED WITH INTERMOLECULAR C-H...O BONDS

Compound	Substituent X	a (Å)	b* (Å)	P (°)	Q (°)	R (°)
o-X benzoylacetylene	Cl	3.21	2.2	167.8	162	145.3
	Br	3.25	2.2	168.3	163	111.0
Propargyl 2-bromo-3-nitrobenzoate	Br	3.39	2.4	163.1	156	148.7

* Based on calculated positions of hydrogen atoms .

The two o-halogenobenzoylacetylenes (I and II) are not isomorphous (although the corresponding benzoic acids are). The difference in packing arises from difference in size of the halogen substituents, which have caused the different arrangement of intermolecular ≡C-H...O bonds. In o-chlorobenzoylacetylene (I), the oxygen lone pair of electrons adjacent to the chlorine atom, is used in hydrogen bonding, leading to infinite chains of the molecules (Fig. 1.5) but in o-bromobenzoylacetylene (II), it is the oxygen lone pair of electrons remote from the Br atom which is utilised for the purpose, causing the close packed zig zag chains of the molecules (Fig. 2.2). Probably this is the reason for which although ≡C $\overset{\wedge}{\ldots}$O=C angles of o-chlorobenzoylacetylene (145.3^{o}) and propargyl 2-bromo-3-nitrobenzoate (148.7^{o}) are similar, the corresponding angle of o-bromobenzoylacetylene (111.0^{o}) is significantly different. In all three cases, the C≡C$\overset{\wedge}{\ldots}$O angles (167.8, 168.3 and 163.1^{o}) are greater than the corresponding ≡C...$\hat{O}$=C angles (145.3, 111.0 and 148.7^{o}).

The ≡C...O separations (3.21 and 3.25) and C≡$\hat{C}$...O (167.8 and 168.3°) in the two o-halogenobenzoylacetylenes (I and II) are similar while the hydrogen bond in propargyl 2-bromo-3-nitrobenzoate (having the corresponding values of 3.39 Å and 163.1° respectively) appears to be comparatively weak. This is also supported by the infra-red investigations which show that the displacement of the ethynyl C-H stretching frequency on going from dilute solution to the solid state is appreciably greater for benzoylacetylene [77 $cm.^{-1}$ (Tyrrell, 1963)] than for the propargyl ester [47 $cm.^{-1}$ (Calabrese, McPhail and Sim, 1967)]. Presumably, the proton donor ability of the acetylinic CH group in the benzoylacetylene is increased, relative to that in the propargyl ester, by conjugation with the carbonyl group, causing a stronger ethynyl hydrogen bond in the former compounds.

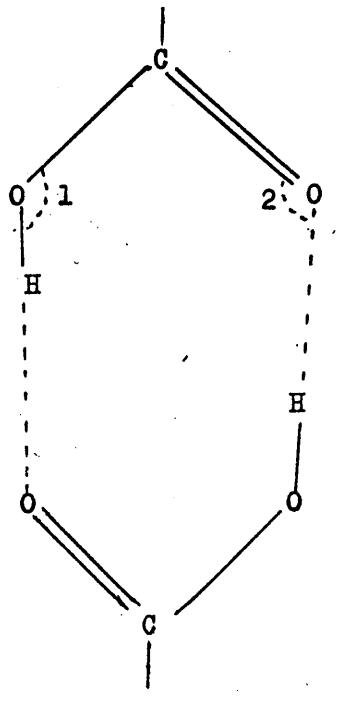
2.5.3 Intermolecular OH...O bond.

In all four o-halogenobenzoic acids (III -VI), centrosymmetric dimers are formed due to the hydrogen bonds between

TABLE 5.2

INTERMOLECULAR O-H...O BONDS IN SOME o-HALOGENOBENZOIC ACIDS .

Substituent	OH...O(Å)	Angle 1(o)	Angle 2(o)
H	2.64	121	120
F	2.583	115.7	121.4
Cl	2.630	112.5	122.9
Br	2.640	112.5	126.9
2-Cl-5-nitro	2.613	113.7	121.5



pair of molecules (See Fig. 3.2). The angles and distances involved in the intermolecular OH...O bonds in these compounds are shown in Table 5.2, which also contains the comparable figures for benzoic acid (Sim, Robertson and Goodwin, 1955). Changing the halogen substituents appears to make no significant difference to the OH...O distances.

2.5.4 Intramolecular overcrowding

From Table 5.3, it is evident that in all 7 compounds (I - VII), the distances of the halogen atoms from the exocyclic carbon and adjacent oxygen atoms are always less than the sums of the corresponding normal van der Waals' radii. This shows that all the molecules might be under some strain.

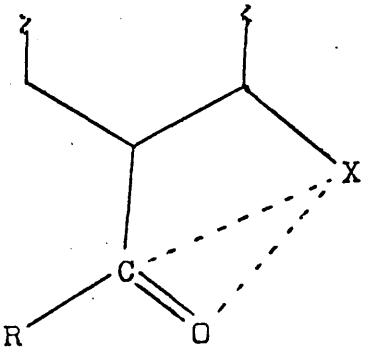
The significant non-planarity of all these compounds is due to the strain of molecular overcrowding caused by the bulky halogen substituents. In all the cases, the strain which would have been imposed on a planar ideal molecule, is relieved in the following ways.

a) The Carboxyl or Carbonyl group, as the case may be,

TABLE 5.3

INTRAMOLECULAR SEPARATIONS AND CORRESPONDING VAN DER WAALS CONTACT DISTANCES (shown in parentheses) IN SOME o-HALOGENO-AROYL COMPOUNDS

Compound	Substituent X	X...C (Å)	X...O (Å)
o-X benzoic acid	F	2.832 (3.35)	2.608 (2.75)
	Cl	3.217 (3.80)	2.892 (3.20)
	Br	3.275 (3.95)	3.004 (3.35)
o-X benzoyl acetylene	Cl	3.178 (3.80)	2.886 (3.20)
	Br	3.279 (3.95)	2.978 (3.35)
2-Cl-5-nitro benzoic acid	Cl	3.173 (3.80)	2.896 (3.20)
2-Cl-1,8-phthaloylnaphthalene	Cl	3.044 (3.80)	2.877 (3.20)



is rotated about the exocyclic $C_{(arom.)}$—$C_{(exocyc.)}$ bond out of the plane of benzene ring so as to increase the separation between the halogen and the adjacent oxygen atoms.

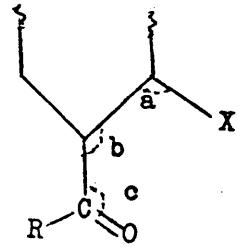
b) The halogen and the exocyclic carbon atoms are displaced in opposite direction out of the plane of the benzene ring.

c) The exocyclic $C_{arom.}$ — $C_{exocyc.}$ and $C_{arom.}$— Halogen bonds are displaced sideways, distorting the normal valency angles, to obtain greater separation between halogen and exocyclic carbon atoms.

Table 5.4 shows that, in a particular series, the extent of rotation of carboxyl (or carbonyl) group plane about the exocyclic C-C bond is increased with increasing size of the halogen substituent. In o-halogenobenzoic acids (III - V), the rotation of this plane is greater than the corresponding halogen substituted benzoylacetylene. Presumably, due to the independent dimer formation through the intermolecular OH...O bond (See Fig. 3.2), this rotation is easily achieved in the former series, whereas in the latter group, comparatively rigid intermolecular chain formation (Fig. 1.5 and 2.2) through≡CH...O link has restricted the twist.

TABLE 5.4

MODE OF THE RELIEF OF INTRAMOLECULAR OVERCROWDING IN SOME o-HALOGENO-AROYL COMPOUNDS



Type of compound	Substituent X	Bond angles in affected regions a(o)	b(o)	c(o)	Carboxyl or carbonyl benzene interplanar angle (o)	Displacements of affected atoms from benzene plane X(Å)	C(Å)	O(Å)
o-X benzoic acid	H	-	120	120	-	-	-	-
	F	120.5	122.5	121.9	10.6	0.002	-0.019	-0.220
	Cl	124.7	122.4	122.2	13.7	0.036	-0.058	-0.323
	Br	124.9	123.4	126.0	18.3	0.064	-0.057	-0.380
o-X benzoylacetylene	Cl	123.1	124.1	124.9	7.1	-0.030	0.033	0.160
	Br	122.1	123.5	124.6	13.6	0.154	-0.062	-0.344
2-Cl-5-nitro benzoic acid	Cl	121.9	125.5	121.3	23.0	-0.001	0.051	0.492
2-Cl-1,8-phthaloyl naphthalene	Cl	121.2	119.8	120.3	42.0	0.160	0.107	0.911

From Tables 5.3 and 5.4 it is evident that although the rotation of the exocyclic group plane with respect to the mean plane through the benzene ring is different, the intramolecular separations of the halogen atoms from the exocyclic carbon and adjacent oxygen atoms of an o-halogenobenzoic acid and corresponding benzoylacetylene are similar. It appears that in the latter series, the strain which would have been imposed by intermolecular hydrogen bond formation, restricting the rotation of the exocyclic group is relieved by accommodating in-plane and out of plane displacement of the affected atoms.

In 2-chloro-5-nitrobenzoic acid (VI), although the situation is rather different, all the three methods (a, b and c) of relieving the strain of intramolecular overcrowding are present. In 2-chloro-1, 8-phthaloylnaphthalene (VII), the situation is entirely different. Here the exocyclic carbon is part of the seven-membered ring. To accommodate the strain of intramolecular overcrowding, the carbonyl oxygen, O(1), is pushed out of the naphthalene plane by 0.911 Å whereas the oxygen atom, O(2), remote from the Cl atom is deviated by only 0.056 Å

[Table 4.9 (b)] and the molecule is buckled (Fig. 4.5).

2.5.5 Conclusion

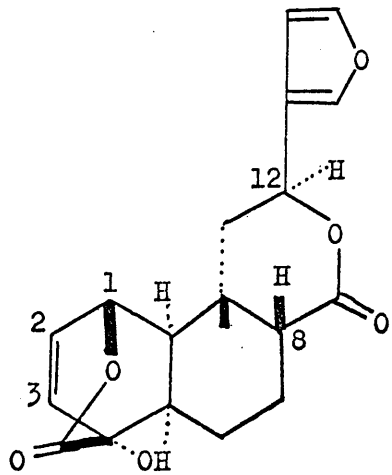
It may, therefore, be concluded that in all the o-halogeno-aroyl compounds (I - VI), the conformation adopted is, (A), with the double bonded oxygen adjacent to the ortho-substituted halogen atom . In the same series, the intramolecular hydrogen bonds are similar. In all the cases (I - VII) the strain of intramolecular overcrowding is relieved by twisting the plane containing the exocyclic group, displacing the affected atoms towards the opposite sides of the plane of the benzene ring and distorting the affected valency angles. In a particular group larger the size of the halogen substituent the greater is the rotation of the carboxyl (or carbonyl) group plane.

SECTION III

CRYSTAL STRUCTURE OF p-BROMOPHENACYL DERIVATIVE OF PALMARIN

3.1 INTRODUCTION

Barton and Elad (1956) assigned constitution (I) for columbin, the main bitter principle of Colombo root. The three other main natural products of the same root have the composition $C_{20}H_{22}O_7$ and are constitutionally 2, 3-epoxy-columbins; these are Jateorin (II), Chasmanthin (III) and Palmarin (IV).



(I)

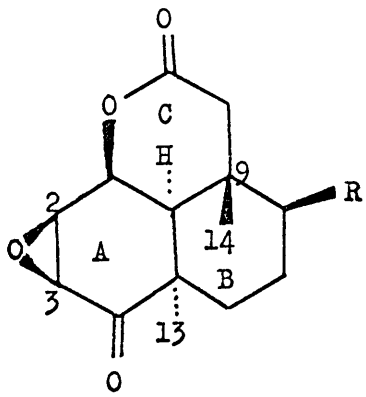
(II) 2, 3-Oxido-I

(III) 2, 3-Oxido-12iso-I

(IV) 2, 3-Oxido-8iso, 12iso-I

The structural relations of these four compounds have already been established by Barton et al. (1962) and Balasubramanian et al. (1962). In the discussion of the stereochemistry of

these Colombo root bitter principles, Overton et al. (1966) suggested the β-epoxide configuration in (V) and hence in palmarin.



(V) R = $-CO_2Me$

(VI) R = $-CO_2CH_2COC_6H_9Br$

In order to establish the extent of their postulated conformational distortion and to confirm the β-epoxide configuration in palmarin, an x-ray crystal structure analysis of the p-bromophenacyl derivative (VI) was carried out. A preliminary communication in this connection, has already been published (Islam, Ferguson, Overton and Melville, 1967).

3.1.1 Crystal data

A p-bromophenacyl derivative of palmarin was crystalised from a mixture of chloroform and toluene. The oscillation and equatorial Weissenberg photographs of the crystal showed that it was orthorhombic. To measure the cell dimensions accurately, a zero layer Weissenberg photograph was taken using Cu Kα radiation ($\lambda = 1.542$ Å). The crystal was then replaced by a thin Al wire and a similar exposure was given to record high order Al powder lines on the same film. 24 spots, on or near either side of the high order Al powder lines were indexed. From a knowledge of the standard $\sin\theta$ values for the lines (Int. Tables, Vol. III, 1962), the corresponding values for these planes were calculated and hence the unit cell constants were computed.

p-Bromophenacyl derivative of palmarin ,

$C_{23}H_{23}O_7Br$, M = 490.9, m.p. = 253°C., orthorhombic, a = 10.755 ± 0.009, b = 8.948 ± 0.007, c = 21.790 ± 0.013 Å, U = 2097 Å^3, Dm = 1.54 gm./cc (by flotation), Z = 4, Dc = 1.554 gm./cc, F(000) = 1008; linear absorption coefficient for Cu Kα radiation ($\lambda = 1.542$ Å), $\mu = 33.3$ cm.$^{-1}$; space group $P2_12_12_1$ (D_2^4, No. 19, Int. Tables, Vol. I, 1965).

3.1.2 Space group

On the Weissenberg photographs of the crystal, rotated around the a-axis, the absence of 00ℓ reflection when ℓ is odd and 0k0 reflection when k is odd was noticed. There were no other systematic absences. The space group is, therefore, either $P2_12_12_1$ or $P22_12_1$. Due to the lack of crystalline material and the unavailability (through breakdown) of a precession camera, photography of the 0k0 reflections was not possible. The presence of a 2_1 screw axis along a was conclusively shown from an examination of the three dimensional Patterson functions and hence the space group is $P2_12_12_1$.

3.1.3 Intensity data

A small piece of the crystal, cut from a larger one, was rotated around a and equi-inclination Weissenberg photographs were taken using the multiple film technique (Robertson, 1943); thus the reciprocal lattice nets $0k\ell - 9k\ell$ were surveyed with Cu Kα radiation ($\lambda = 1.542$ Å). Visual estimation by comparison with a calibrated step wedge led to 1907 independent reflections. The

individual layers of the intensity data were put approximately on the same scale by making use of the known exposure times. The intensity data were then corrected for the appropriate Lorentz, polarisation and rotation factors (See I, 1. 3, 3) and the absorption corrections were ignored.

The following analysis shows the wide range of the intensity data collected for the structure analysis.

$\|F\|$obs	Sin θ/λ				Total
	0.0 - 0.2	0.2 - 0.4	0.4 - 0.6	0.6 - 0.8	
0 - 15	3	79	565	164	811
15 - 31	11	193	437	18	659
31 - 61	27	219	100	-	346
61 - 123	32	54	-	-	86
123 - 200	4	1	-	-	5
Total	77	546	1102	182	1907

The ratio of the square of the atomic number of the heavy atom to the sum of the squares of the atomic numbers of the light atoms per crystal asymmetric unit,

$$\gamma = f_H^2 \Big/ \Sigma f_R^2 = 0.94 \qquad (1)$$

is near to the ideal value of one, as suggested by Lipson and Cochran (1966) and is assumed to be favourable for the heavy atom method of structure solution.

During structure factor calculations, the different layers of intensity data were scaled so as to make $K \Sigma |F_o|$ equal to $\Sigma |F_c|$. Subsequently the various layer-scale-factors were refined by least squares methods.

3.1.4 Structure determination

Sections of the three dimensional Patterson functions at u = 0 and 0.5, v = 0.5 and w = 0.5 were computed and dominating Br-Br vector peaks were obtained in the three sections, u = v = w = 0.5 (Fig. 1.1). In the section at u = 0, no significant peak was noticed. The positions of the Br-Br vector peaks in the three Harker sections were then calculated by Booth's method (Booth, 1948 a) and from these the fractional co-ordinates for the heavy atom was found to be (0.223, 0.25 and 0.093).

To avoid the selection of the planes having no contribution from the Br atom (at y = 0.25) and to achieve a better result from the heavy atom method, 3 cycles of Fourier synthesis were

computed with the Fourier co-efficients multiplied by a weight, proportional to the probability that the phase being applied to each co-efficient is correct (Woolfson, 1956; Sim, 1960). Due to the large number of high order reflections and the good quality of the intensity data, in the first three dimensional electron density distribution all the 31 non-hydrogen atomic peaks and their pseudo images were revealed; out of these 19 atomic locations [Br, O(1) to O(4), O(6), O(7), C(1) to C(5), C(12), C(16), C(17), C(20) to C(23)] were well identifiable. (For numbering scheme see Fig. 1.2). The peak locations of these atoms were then computed using "Fourier search program" (McGregor, 1966). In the next electron density distribution the positions of all the heavier atoms were obtained with the exception of O(5), C(13) and C(15). One further cycle of electron density synthesis revealed the locations of all the 31 non-hydrogen atoms.

In the fourth cycle of structure factor and electron density synthesis, improved locations for these atoms were obtained. The residual, R, at this stage was 0.21. The course of the structure solution is shown in Table 1.1.

In the difference Fourier synthesis no significant features were noticed indicating the correctness of the structure. Two three dimensional electron density distributions were computed using F_o as Fourier coefficient in one case and F_c in the other and the peak positions for all the 31 atoms were calculated from both maps. Backshift corrections (Booth, 1946 b) were then applied to minimise series termination errors (See Sec. I, 1.7.1.1).

The structure amplitudes were then placed on an approximate absolute scale by ensuring that $K\Sigma|F_o| = \Sigma|F_c|$ for each layer.

In the structure factor calculations, the atomic scattering curves used, were those of Int. Tables, Vol. III (1962), and same value of (Uiso = 0.044) was allotted for all non-hydrogen atoms.

3.1.5 Structure refinement by the least squares methods

Altogether 12 cycles of least squares refinement were done using a block diagonal approximation to adjust the atomic parameters of p-bromophenacyl derivative of palmarin, at the end of which the parameter shifts were very small and much less than

one third of the corresponding estimated standard deviations indicating the convergence of the refinement.

In the first cycle of least squares refinement adjustments were made for the individual layer scale factors, positional and isotropic thermal parameters of the non-hydrogen atoms using unit weight for all data. In the subsequent cycles, the weighting scheme used, was that of Cruickshank et al.(1961) i.e.

$$\sqrt{w} = 1/(p_1 + |F| + p_2|F|^2 + p_3|F|^3)^{\frac{1}{2}} \qquad (2)$$

starting with $p_1 = 2\left|F_o\right|_{min.} = 1.5$, $p_2 = 2/\left|F_o\right|_{max.} = 0.036$ and $p_3 = 0$.(Cruickshank, 1964), ensuring the average similar $\sum w\Delta^2$ in all batches of data, grouped in the order of increasing $\left|F_o\right|$ and $\sin\theta/\lambda$, the final values of these constants were adjusted to 3, 0.12 and 0.0015 respectively.

After the first cycle of refinement, the intensity data were scaled with the refined individual layer scale factors and the refinement was continued. At the end of the fifth cycle no appreciable change in the atomic parameters was noticed. The residual, R, was 0.124. A three dimensional difference

synthesis was then computed which revealed anisotropic vibrational characteristics of the non-hydrogen atoms. Apart from the 6 hydrogen atoms of the two methyl groups, the peaks of all the hydrogen atoms were also noticed and there were no other significant features.

The intensity data were then placed on a common absolute scale using the values of the scale factors from cycle 5. Thereafter the refinement of an overall scale factor, positional and anisotropic thermal parameters was continued. After the eighth cycle the locations of 17 non-methyl hydrogen atoms were deduced from geometrical considerations and were introduced, but not refined, in subsequent cycles. The isotropic thermal vibrations allotted to the hydrogen atoms were those of the carbon atoms to which these are bonded.

At the end of the twelfth cycle of refinement, the shifts of the atomic parameters were quite negligible in comparison with the appropriate estimated standard deviations. This showed the convergence of the structure refinement. Structure factors were then calculated with the refined non-hydrogen atomic parameters

and the three dimensional difference synthesis was computed. In the resultant map peaks corresponding to the 17 non-methyl hydrogen atoms were revealed in the expected positions and diffuse positive regions were noticed near to the two methyl carbon atoms; the exact locations of the corresponding hydrogen atoms were not identifiable. No other significant features were noticed and hence the refinement was concluded. The final value of the residual, R, is 0.078.

In all the structure factor calculations, the atomic scattering curves used for different atoms were those of Int. Tables Vol. III, (1962).

3.1.6 Final atomic parameters, molecular dimensions etc.

The composite final electron density synthesis viewed down the a-axis and the numbering scheme of the atoms are shown in Fig. 1.2 and the corresponding arrangement of the molecules in the cell can be seen in Fig. 1.3. The bond lengths and angles are in Figs. 1.4a and 1.4b respectively. The deformation of the molecule is shown through a special projection in Fig. 1.5.

The final agreement of the structure amplitudes is shown in Table 1.3. The fractional co-ordinates with estimated standard deviations of the non-hydrogen atoms are in Table 1.4, the corresponding orthogonal co-ordinates and estimated standard deviations (in $\mathring{A}$) are given in Table 1.5. The calculated fractional co-ordinates of the non-methyl hydrogen atoms are presented in Table 1.6. The anisotropic temperature factors are represented in terms of the values of U_{ij} (See Sec.I, 1.3.2) in Table 1.7, and in Table 1.8 there are the principal values of the vibration tensors, and their direction cosines referred to the crystal axes. The intramolecular and intermolecular short distances are shown in Table 1.9. Displacements of atoms from various mean planes can be seen in Table 1.10.

The final estimated standard deviations of the average carbon-carbon, carbon-oxygen and carbon-bromine bond lengths are 0.011, 0.010 and 0.007 $\mathring{A}$ respectively. The average estimated standard deviation of the valency angles is 0.7°.

DIAGRAMS AND TABLES

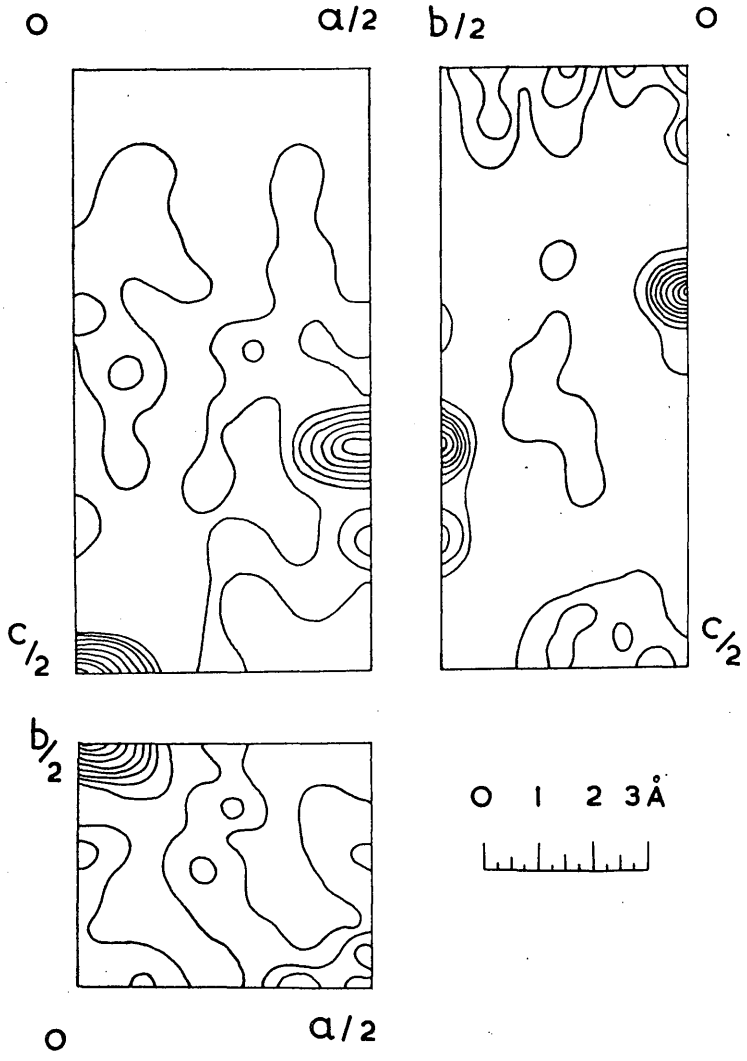


FIG. 1.1

The Harker sections at u = 0.5, v = 0.5 and w = 0.5. Contours are at arbitrary intervals.

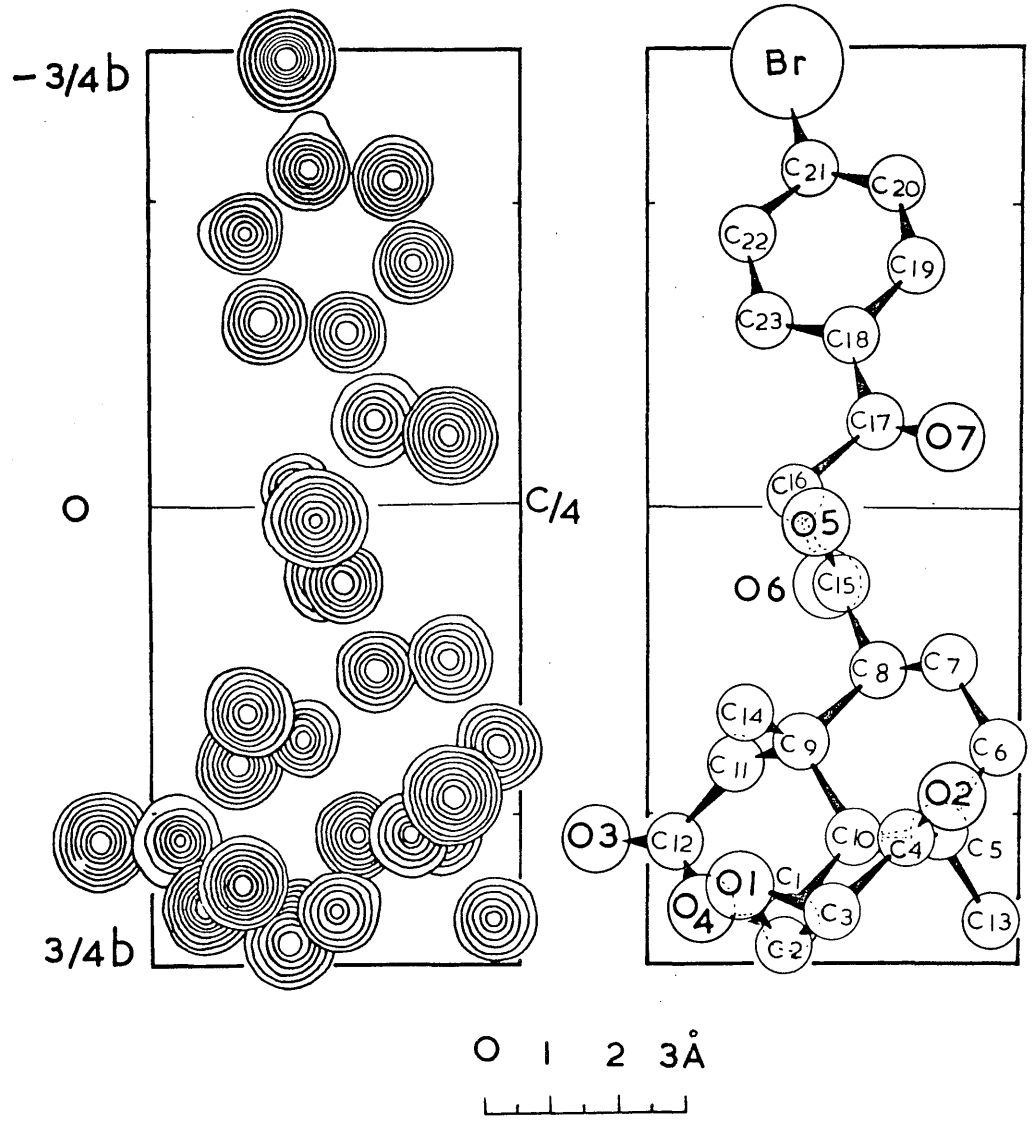


FIG. 1.2

The composite final electron density synthesis viewed down the a-axis and the numbering scheme used for identifying the non-hydrogen atoms (the numbering of a hydrogen atom is started with the figure for the carbon atom to which it is bonded). Contours are at 1 e/Å^3 intervals except around Br (4 e/Å^3) starting at the one electron level.

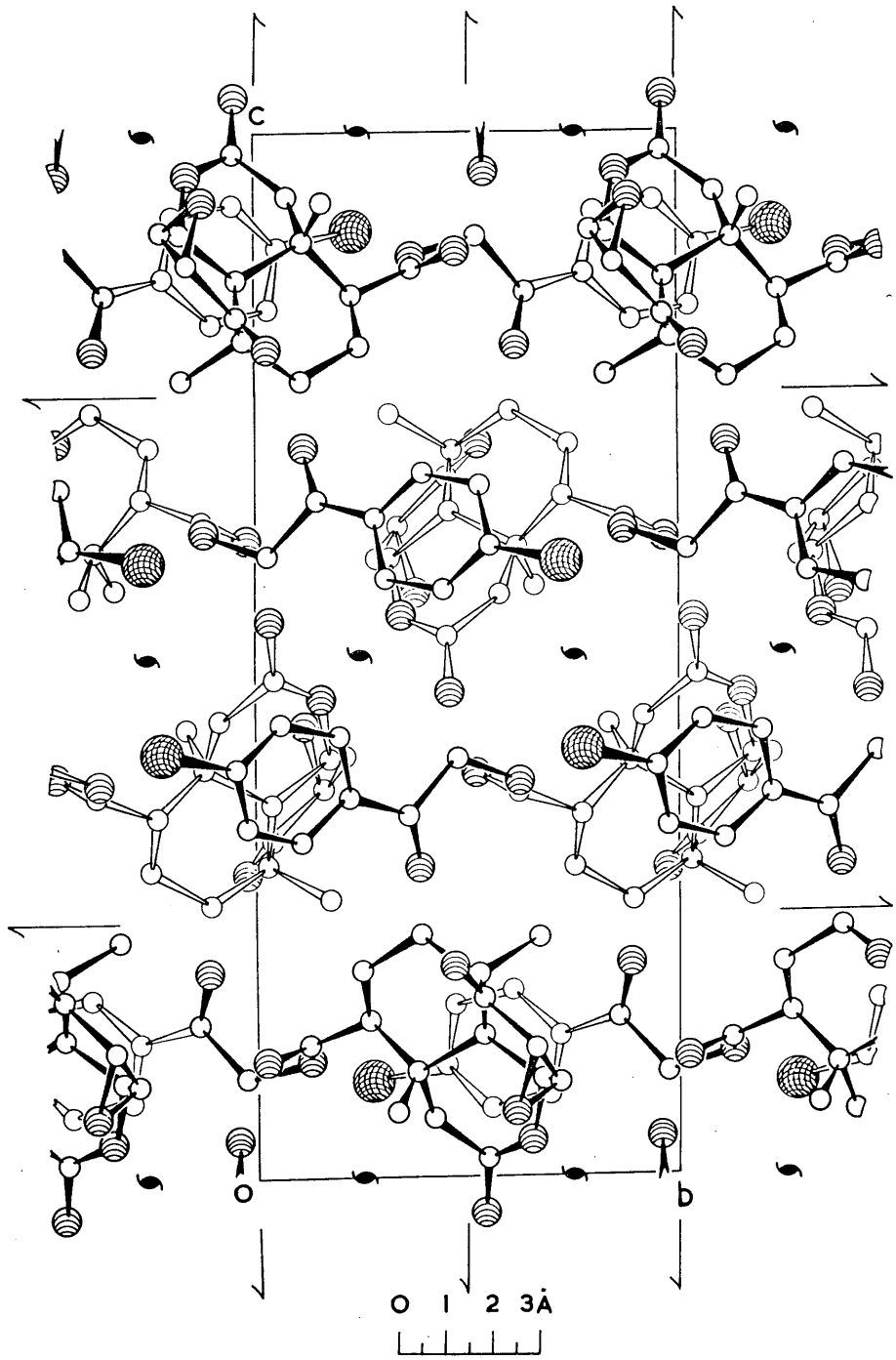


FIG. 1.3

The molecular packing viewed down the a-axis. The regions above 5.76 Å are shown in solid lines.

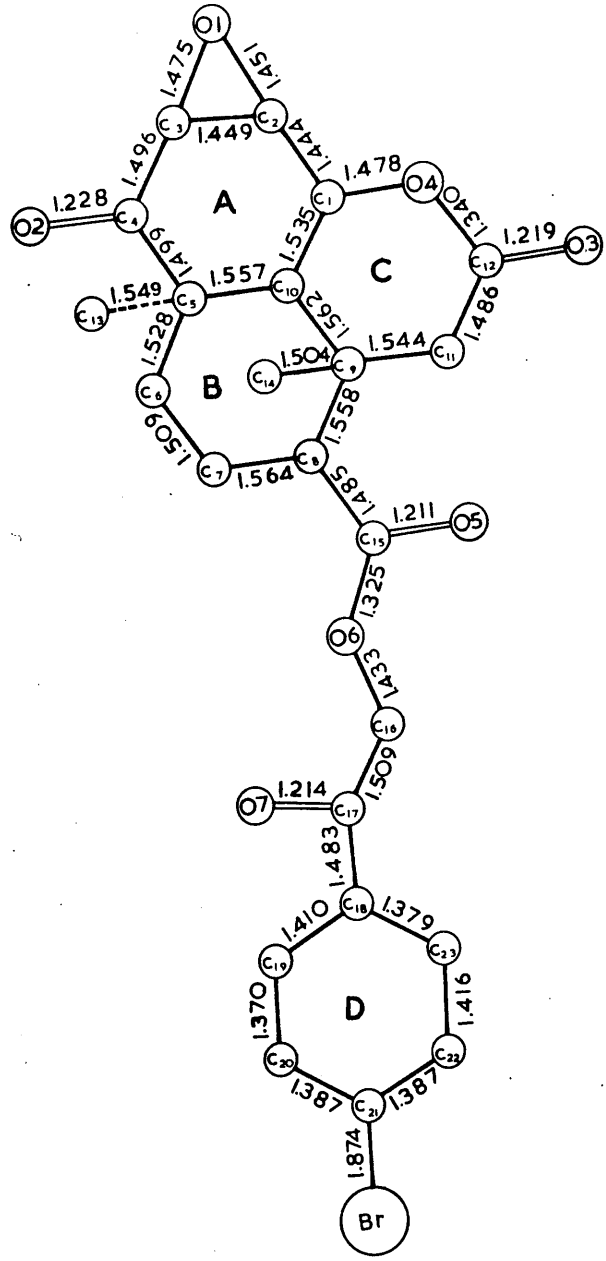


FIG. 1.4a

The molecular diagram showing the lengths (in Å) of the valency bonds.

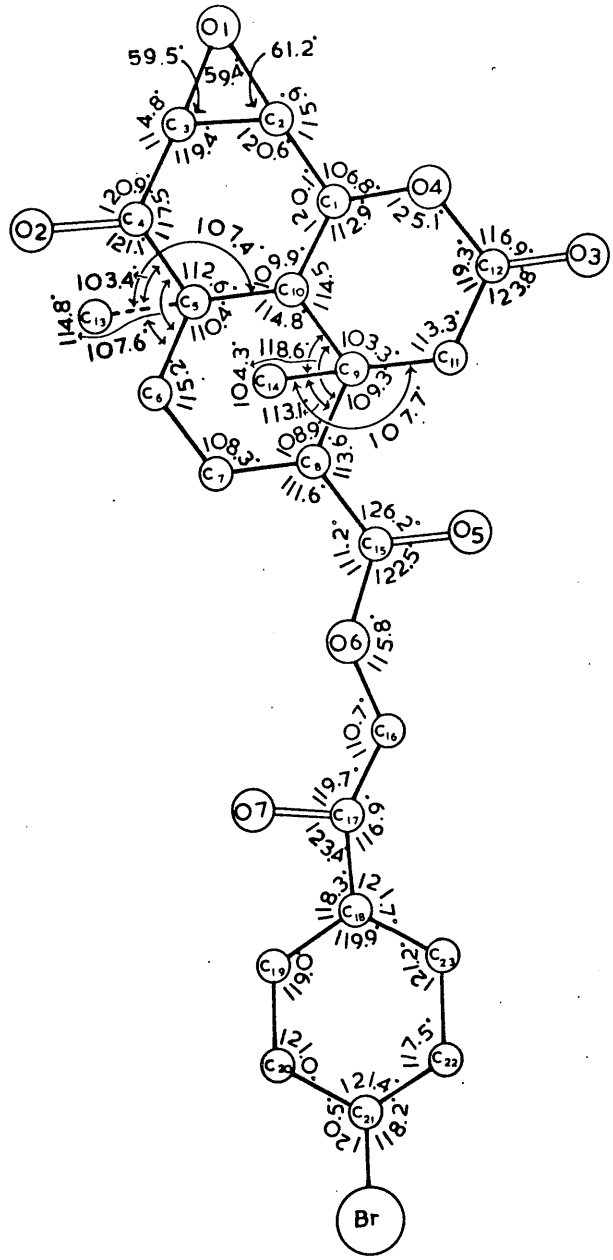


FIG. 1.4b

The molecular diagram showing the valency angles (in degrees).

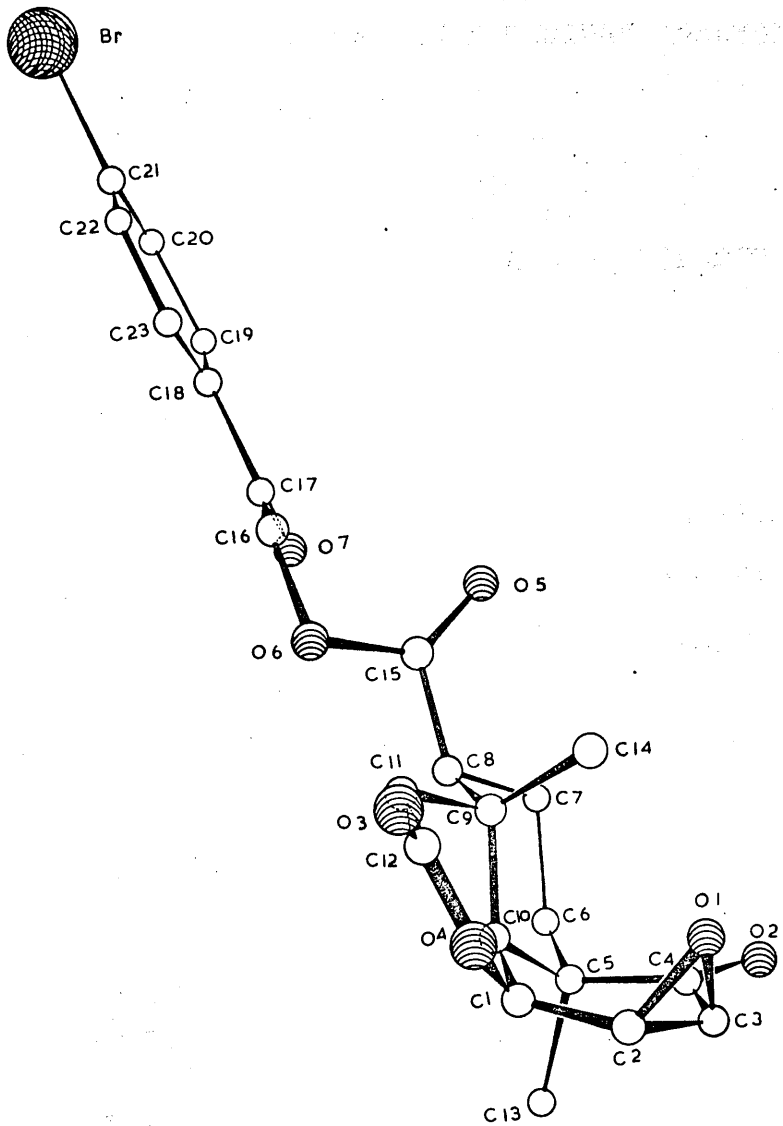


FIG. 1.5

The special view of a molecule showing the deformations.

TABLE 1.1

COURSE OF THE STRUCTURE ANALYSIS

OPERATION	ATOMS INCLUDED	R FACTOR
Three Harker sections at u=v=w=0.5	Br	-
Structure factor calculations and electron density synthesis	Br, O(1) to O(4),O(6), O(7),C(1) to C(5),C(12), C(16),C(17) and C(20) to C(23)	0.51
-Do-	Br, O(1) to O(4), O(6), O(7),C(1) to C(12),C(14), C(16) to C(23)	0.36
-Do-	All non-hydrogen atoms	0.30
-Do-	Improved locations of all the 31 atoms	0.25
Structure factor calculations		0.21

TABLE 1.2

PROGRESS OF THE REFINEMENT

Cycle	R factor	$\Sigma w\Delta^2$	$R'=\Sigma w\Delta^2/\Sigma w\|Fo\|^2$
1[a]	0.226	102918.0	0.057
2[b]	0.151	1234.5	0.058
3	0.127	700.9	0.028
4	0.124	656.7	0.027
5[c]	0.124	649.8	0.027
6	0.092	317.7	0.016
7	0.085	254.6	0.013
8[d]	0.082	204.5	0.011
9	0.077	166.7	0.011
10[e]	0.077	156.3	0.011
11	0.078	111.1	0.011
12	0.078	108.1	0.011

a) Adjustment of individual layer scales , positional and isotropic thermal parameters using unit weight for all data .

b) Data scaled and refinement continued using a specific weighting scheme .

c) Difference synthesis ; |Fo| scaled; refinement of an overall scale facor, positional and anisotropic thermal parameters .

d) 17 Hydrogen atoms introduced and weighting adjusted .

e) Weighting scheme further adjusted .

TABLE 1.3

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

H	K	L	|Fo|	|Fc|	H	K	L	|Fo|	|Fc|	H	K	L	|Fo|	|Fc|	H	K	L	|Fo|	|Fc|	H	K	L	|Fo|	|Fc|
0	0	6	117.1	137.1	0	5	15	32.3	32.5	1	1	3	115.3	138.1	1	5	15	20.5	20.2	2	0	10	48.0	53.4	2	4	21	7.5	6.8
0	0	8	38.4	35.6	0	5	16	28.9	27.7	1	1	4	80.8	83.5	1	5	16	14.2	14.0	2	0	11	14.5	12.5	2	4	22	6.1	6.3
0	0	10	74.5	78.2	0	5	17	21.7	22.2	1	1	5	43.5	43.7	1	5	17	7.1	6.2	2	0	12	43.0	45.0	2	4	25	6.7	5.9
0	0	12	14.0	14.7	0	5	18	9.5	10.2	1	1	6	30.1	30.1	1	5	18	4.0	4.5	2	0	13	32.2	28.2	2	5	0	17.2	14.2
0	0	14	31.7	29.3	0	5	19	16.0	17.6	1	1	7	79.7	85.2	1	5	19	10.2	10.2	2	0	14	35.7	34.1	2	5	1	61.8	59.6
0	0	16	32.5	33.1	0	5	20	13.6	14.5	1	1	8	15.2	13.3	1	5	23	14.1	12.6	2	0	15	15.2	14.6	2	5	2	14.4	12.3
0	0	18	25.5	21.9	0	5	21	14.8	15.1	1	1	9	61.6	70.5	1	5	24	5.9	5.9	2	0	16	57.5	55.0	2	5	3	17.5	16.3
0	0	20	23.9	21.8	0	5	22	6.8	6.4	1	1	10	37.2	35.6	1	6	0	7.0	6.5	2	0	17	24.6	23.6	2	5	4	36.6	40.2
0	0	22	14.6	12.6	0	6	0	38.5	35.5	1	1	11	30.5	30.4	1	6	1	47.8	44.3	2	0	18	10.0	8.3	2	5	5	52.3	58.7
0	0	24	9.3	7.9	0	6	2	9.9	9.1	1	1	12	12.8	10.8	1	6	2	55.0	56.9	2	0	19	6.2	8.0	2	5	6	25.1	25.5
0	0	26	12.9	12.4	0	6	3	38.3	38.4	1	1	13	67.5	73.2	1	6	3	20.2	19.8	2	0	20	26.0	24.0	2	5	7	24.9	29.1
0	1	2	104.6	121.6	0	6	4	31.3	31.2	1	1	14	12.4	10.1	1	6	4	49.9	50.7	2	0	22	16.4	14.9	2	5	8	20.1	20.2
0	1	3	31.4	33.4	0	6	5	11.8	10.6	1	1	15	32.0	32.2	1	5	5	18.7	18.7	2	0	24	7.1	6.0	2	5	9	28.5	30.7
0	1	4	6.5	9.0	0	6	6	26.7	32.1	1	1	16	18.9	18.0	1	6	6	18.2	18.4	2	0	26	6.8	5.7	2	5	10	30.3	30.4
0	1	5	88.6	100.0	0	6	7	13.9	15.2	1	1	17	33.0	30.8	1	6	7	19.6	20.1	2	1	2	65.1	65.5	2	5	11	45.5	50.2
0	1	6	71.0	79.9	0	6	8	7.1	6.8	1	1	18	16.1	14.1	1	6	8	36.1	42.1	2	1	3	99.0	97.6	2	5	12	12.0	9.3
0	1	7	37.2	36.0	0	6	9	10.2	8.8	1	1	19	37.7	35.2	1	6	9	21.4	23.8	2	1	4	67.0	64.0	2	5	13	12.2	12.4
0	1	9	54.9	61.5	0	6	10	25.0	28.8	1	1	20	14.2	11.2	1	6	11	29.1	32.0	2	1	5	74.4	68.3	2	5	14	25.5	25.4
0	1	10	49.4	50.7	0	6	12	20.3	22.6	1	1	21	14.6	11.5	1	6	12	27.1	28.3	2	1	6	46.1	50.4	2	5	15	39.3	44.7
0	1	11	64.3	71.7	0	6	13	15.7	18.3	1	1	23	20.6	17.2	1	6	13	14.2	15.4	2	1	7	43.7	46.7	2	5	17	17.5	17.6
0	1	12	10.3	9.2	0	6	14	7.6	6.0	1	1	24	7.8	7.7	1	6	14	25.3	27.3	2	1	8	14.7	15.0	2	5	18	8.1	8.5
0	1	13	10.4	10.0	0	6	16	12.8	13.9	1	1	25	16.3	13.8	1	6	15	23.8	25.1	2	1	9	33.6	34.6	2	5	19	8.7	8.4
0	1	14	9.7	8.9	0	6	17	14.4	14.4	1	2	0	31.4	26.3	1	6	16	6.9	7.2	2	1	10	30.0	28.9	2	5	20	9.0	10.4
0	1	15	37.7	36.4	0	6	18	4.0	2.2	1	2	1	51.7	45.3	1	6	17	13.5	14.0	2	1	11	58.4	62.8	2	5	21	13.3	14.2
0	1	17	21.9	21.0	0	6	19	5.4	5.8	1	2	2	65.0	72.6	1	6	18	16.3	17.8	2	1	12	29.5	29.8	2	5	22	6.3	6.6
0	1	18	21.3	18.8	0	6	20	10.0	10.1	1	2	3	59.1	59.6	1	6	19	5.0	5.2	2	1	13	19.4	19.4	2	5	23	9.6	9.0
0	1	19	22.6	18.3	0	6	21	7.9	8.2	1	2	4	64.4	69.7	1	6	20	13.6	12.9	2	1	14	15.5	14.2	2	5	24	8.9	8.0
0	1	20	7.6	7.4	0	6	22	6.4	6.0	1	2	5	15.3	12.4	1	6	21	12.8	11.7	2	1	15	24.4	28.1	2	6	0	34.2	30.0
0	1	21	18.3	16.1	0	6	23	5.8	5.2	1	2	6	71.5	78.8	1	6	22	7.5	7.2	2	1	16	13.4	11.5	2	6	1	23.8	20.2
0	1	22	11.1	10.3	0	7	1	66.5	63.9	1	2	7	58.0	62.5	1	7	0	41.6	35.1	2	1	17	30.3	30.8	2	6	2	36.1	32.9
0	1	27	12.1	10.2	0	7	2	52.8	48.9	1	2	8	79.1	86.0	1	7	1	20.3	16.6	2	1	18	16.4	16.7	2	6	4	34.1	33.8
0	2	0	28.1	20.2	0	7	3	14.4	12.9	1	2	9	34.6	37.4	1	7	2	21.8	18.1	2	1	19	11.8	9.5	2	6	5	29.9	25.3
0	2	1	28.5	20.8	0	7	4	25.5	25.0	1	2	10	13.6	14.7	1	7	3	37.1	39.1	2	1	21	24.3	21.5	2	6	6	27.8	30.1
0	2	2	39.1	36.8	0	7	5	41.8	43.9	1	2	12	36.8	41.3	1	7	4	29.1	30.7	2	1	22	17.7	17.6	2	6	7	11.6	10.8
0	2	3	41.1	46.5	0	7	6	28.6	28.4	1	2	13	31.5	29.5	1	7	5	19.9	19.5	2	1	23	7.5	6.6	2	6	8	11.8	14.7
0	2	4	64.2	73.5	0	7	7	9.6	8.4	1	2	14	41.5	41.4	1	7	6	34.1	31.6	2	1	25	8.3	7.3	2	6	9	14.5	13.8
0	2	5	22.3	24.9	0	7	8	20.3	25.7	1	2	15	20.7	21.4	1	7	7	27.7	26.9	2	1	26	7.7	5.4	2	6	10	28.5	31.7
0	2	6	98.9	114.6	0	7	9	27.5	31.1	1	2	16	17.7	16.3	1	7	8	5.8	4.3	2	1	27	10.8	10.1	2	6	11	10.1	9.3
0	2	8	16.3	13.8	0	7	10	17.4	16.9	1	2	17	21.0	19.2	1	7	9	25.1	31.1	2	2	0	106.7	109.3	2	6	12	17.1	19.9
0	2	9	34.4	36.4	0	7	11	11.5	11.2	1	2	18	20.7	18.0	1	7	10	16.4	18.5	2	2	1	33.7	27.7	2	6	13	21.3	20.5
0	2	10	36.9	42.1	0	7	14	17.9	18.3	1	2	20	29.2	28.1	1	7	11	12.3	13.7	2	2	2	25.5	22.2	2	6	15	13.0	13.7
0	2	11	3.2	4.0	0	7	15	18.8	20.4	1	2	21	8.0	7.9	1	7	12	18.2	18.4	2	2	3	60.6	57.6	2	6	16	19.8	21.3
0	2	12	50.5	54.4	0	7	16	11.8	7.4	1	2	22	12.9	11.6	1	7	13	17.1	18.1	2	2	4	25.4	29.1	2	6	19	10.6	11.9
0	2	13	14.8	14.2	0	7	17	14.6	15.1	1	2	23	9.7	9.2	1	7	14	7.9	7.2	2	2	5	27.2	23.6	2	6	20	16.4	18.5
0	2	14	9.2	7.8	0	7	18	6.1	5.7	1	2	24	22.5	19.7	1	7	15	16.3	16.0	2	2	6	71.9	82.3	2	6	21	5.9	6.8
0	2	15	19.6	19.7	0	7	20	5.1	4.5	1	3	0	39.0	32.0	1	7	16	12.8	13.3	2	2	7	41.3	42.4	2	7	0	30.4	25.2
0	2	16	50.0	49.5	0	7	21	17.3	16.3	1	3	1	53.1	53.2	1	7	17	5.0	5.4	2	2	8	44.3	46.7	2	7	1	44.0	39.9
0	2	17	19.8	19.4	0	8	0	44.6	42.1	1	3	2	46.2	48.1	1	7	18	9.9	8.9	2	2	9	14.1	13.3	2	7	2	30.6	29.8
0	2	18	22.1	20.8	0	8	1	21.7	18.2	1	3	3	102.3	114.2	1	7	19	9.6	8.6	2	2	10	70.3	77.8	2	7	3	12.7	10.8
0	2	19	19.0	15.1	0	8	2	7.5	6.8	1	3	4	46.4	48.2	1	7	20	10.5	9.6	2	2	11	31.4	32.5	2	7	4	25.6	24.7
0	2	20	20.4	18.2	0	8	3	21.4	19.8	1	3	5	63.0	62.5	1	7	21	6.1	5.3	2	2	12	42.5	43.5	2	7	5	15.8	14.4
0	2	21	18.6	15.6	0	8	4	30.5	29.7	1	3	6	34.1	32.6	1	8	0	14.8	12.0	2	2	13	9.9	10.7	2	7	6	6.2	7.9
0	2	22	25.1	24.9	0	8	5	15.1	14.4	1	3	7	80.2	94.5	1	8	1	12.3	8.2	2	2	16	21.7	21.6	2	7	7	23.0	28.4
0	3	1	83.0	92.6	0	8	6	12.3	12.5	1	3	8	7.5	5.3	1	8	2	13.4	13.6	2	2	15	22.9	23.0	2	7	8	25.6	25.1
0	3	2	61.2	64.5	0	8	7	14.7	14.4	1	3	9	51.2	54.5	1	8	3	8.2	7.1	2	2	16	43.5	46.4	2	7	9	11.0	11.4
0	3	3	13.4	11.8	0	8	8	11.4	11.4	1	3	10	14.6	14.1	1	8	4	28.8	25.8	2	2	18	11.7	10.7	2	7	10	11.8	12.2
0	3	4	122.6	142.4	0	8	9	9.6	9.4	1	3	11	20.9	21.7	1	8	5	30.2	28.5	2	2	19	18.2	17.9	2	7	11	15.0	15.9
0	3	5	19.6	14.4	0	8	10	25.8	24.9	1	3	12	9.1	9.4	1	8	7	21.6	19.5	2	2	20	21.1	21.3	2	7	13	8.1	8.1
0	3	6	13.4	10.7	0	8	13	16.2	13.1	1	3	13	44.3	48.6	1	8	8	23.7	22.0	2	2	21	9.1	8.1	2	7	14	9.7	10.5
0	3	7	52.3	59.6	0	8	14	10.0	7.5	1	3	14	21.7	20.0	1	8	9	12.1	11.5	2	2	22	19.5	17.0	2	7	15	10.2	9.7
0	3	8	49.8	50.1	0	8	15	8.8	7.6	1	3	15	10.9	8.9	1	8	10	13.8	14.5	2	2	26	9.6	8.5	2	7	17	17.5	17.3
0	3	9	24.8	19.8	0	8	16	12.2	12.4	1	3	16	5.6	5.4	1	8	11	22.4	22.0	2	3	0	43.3	35.9	2	7	21	17.1	15.7
0	3	11	66.8	67.2	0	8	19	12.9	11.4	1	3	17	23.6	22.2	1	8	12	12.0	11.9	2	3	1	63.5	57.0	2	8	0	21.3	19.8
0	3	13	11.9	9.7	0	9	1	11.2	11.5	1	3	18	24.6	26.6	1	8	13	9.8	10.0	2	3	2	47.9	51.2	2	8	1	39.4	35.7
0	3	14	30.5	26.5	0	9	2	8.4	6.9	1	3	19	19.2	16.2	1	8	14	18.7	17.8	2	3	4	11.2	10.8	2	8	2	25.7	23.1
0	3	15	22.3	25.4	0	9	3	15.1	14.6	1	3	21	11.7	9.3	1	8	17	8.2	8.2	2	3	5	15.8	9.3	2	8	3	42.1	41.8
0	3	16	19.3	18.8	0	9	4	11.8	10.5	1	3	22	11.2	10.5	1	8	18	9.4	8.8	2	3	6	64.3	67.9	2	8	4	26.4	24.8
0	3	17	44.2	42.9	0	9	5	24.9	22.4	1	3	23	18.5	16.9	1	9	0	30.8	29.5	2	3	7	26.7	27.2	2	8	5	22.0	22.0
0	3	18	10.7	10.3	0	9	7	11.4	10.6	1	3	25	10.2	9.0	1	9	1	18.2	16.5	2	3	7	33.3	32.8	2	8	6	16.1	15.3
0	3	19	4.4	3.2	0	9	8	17.3	16.0	1	4	0	14.0	9.8	1	9	2	13.7	10.6	2	3	8	38.7	39.2	2	8	7	20.3	20.9
0	3	20	18.8	16.4	0	9	9	17.7	16.2	1	4	1	48.6	44.6	1	9	3	16.9	18.2	2	3	9	30.1	30.9	2	8	8	9.2	9.2
0	3	21	22.1	20.4	0	9	10	17.6	17.2	1	4	2	76.3	80.1	1	9	4	13.6	13.6	2	3	10	11.2	11.4	2	8	9	12.2	11.5
0	3	25	8.1	6.1	0	9	11	17.7	18.2	1	4	3	26.4	22.7	1	9	5	11.0	10.0	2	3	11	30.6	36.1	2	8	10	22.7	23.2
0	4	0	74.8	65.1	0	9	14	20.9	20.2	1	4	4	82.3	91.1	1	9	6	16.3	12.9	2	3	12	29.7	29.4	2	8	12	11.5	12.1
0	4	1	11.9	9.0	0	9	15	11.1	11.9	1	4	5	30.0	30.3	1	9	7	9.5	9.1	2	3	13	16.4	18.1	2	8	13	13.8	14.7
0	4	2	20.0	21.4	0	10	0	16.8	16.3	1	4	6	24.1	22.8	1	9	8	6.4	5.3	2	3	14	19.9	19.8	2	8	14	13.7	14.7
0	4	3	15.2	13.3	0	10	1	9.7	8.7	1	4	7	47.0	48.4	1	9	9	13.6	13.4	2	3	15	22.7	19.7	2	8	15	12.5	12.2
0	4	4	55.1	59.9	0	10	2	7.3	7.2	1	4	8	56.7	71.1	1	9	10	13.6	12.0	2	3	16	36.5	35.3	2	8	16	14.6	15.4
0	4	5	27.1	23.5	0	10	3	13.0	12.2	1	4	9	25.2	24.2	1	9	13	14.0	12.4	2	3	17	43.0	40.9	2	8	19	14.3	13.7
0	4	6	24.3	28.5	0	10	4	6.2	6.5	1	4	10	10.8	11.0	1	9	14	5.7	6.0	2	3	18	21.3	20.8	2	9	1	20.8	19.6
0	4	7	11.6	10.6	0	10	5	9.3	8.0	1	4	11	33.2	32.0	1	9	15	4.5	4.8	2	3	19	8.3	9.3	2	9	2	14.4	14.0
0	4	8	10.0	10.1	0	10	6	3.4	2.4	1	4	12	32.1	31.9	1	9	16	8.1	7.5	2	3	20	7.1	6.7	2	9	3	17.7	15.6
0	4	9	29.4	24.6	0	10	7	11.5	12.6	1	4	13	12.0	10.7	1	10	1	23.5	22.5	2	3	21	16.5	17.5	2	9	4	7.6	7.6
0	4	10	66.0	72.6	0	10	9	17.1	16.0	1	4	14	31.1	35.5	1	10	2	13.6	12.6	2	3	22	7.5	6.7	2	9	5	25.6	26.0
0	4	11	21.8	19.4	0	10	10	5.0	5.4	1	4	15	14.7	15.8	1	10	3	7.6	5.7	2	3	23	9.2	10.1	2	9	6	12.2	11.4
0	4	12	35.9	41.9	0	11	2	17.7	15.0	1	4	16	20.7	19.7	1	10	4	12.9	13.2	2	4	0	114.7	110.3	2	9	7	8.5	8.2
0	4	13	9.0	7.9	0	11	6	12.4	10.7	1	4	18	20.1	21.0	1	10	5	16.4	16.0	2	4	1	14.0	15.6	2	9	8	13.8	16.6
0	4	14	12.4	11.2	1	0	3	39.3	41.1	1	4	19	14.6	13.3	1	10	6	11.5	10.5	2	4	2	26.6	25.7	2	9	9	13.8	17.7
0	4	15	17.0	14.6	1	0	4	64.5	73.9	1	4	20	15.7	14.6	1	10	7	9.3	9.3	2	4	4	34.3	37.7	2	9	10	7.8	8.1
0	4	16	48.3	48.4	1	0	5	75.5	80.1	1	4	21	14.5	13.6	1	10	8	18.4	18.4	2	4	4	71.6	77.4	2	9	11	17.5	17.3
0	4	17	12.3	13.0	1	0	6	38.3	30.5	1	4	24	10.8	11.4	1	10	11	14.3	12.4	2	4	5	6.6	5.5	2	9	12	9.1	9.1
0	4	18	20.0	19.9	1	0	8	56.2	64.0	1	5	0	33.1	27.6	1	10	12	8.1	8.0	2	4	6	50.2	54.6	2	9	14	12.8	12.6
0	4	20	22.5	18.5	1	0	9	33.3	32.6	1	5	1	38.6	35.2	1	11	0	15.6	13.9	2	4	7	22.7	24.5	2	9	15	15.5	14.2
0	4	22	17.6	14.6	1	0	10	66.4	71.3	1	5	2	15.3	12.3	1	11	1	8.5	8.0	2	4	8	24.6	27.2	2	10	0	22.7	22.5
0	5	1	46.5	47.0	1	0	11	6.4	7.4	1	5	3	52.0	55.0	1	11	2	6.4	6.1	2	4	9	20.3	21.0	2	10	1	6.8	7.2
0	5	2	63.0	65.0	1	0	12	37.7	41.2	1	5	5	47.2	46.8	1	11	3	16.9	16.9	2	4	10	36.7	36.6	2	10	2	10.7	10.0
0	5	3	37.2	35.9	1	0	13	9.7	9.5	1	5	6	43.5	45.7	1	11	4	10.2	9.0	2	4	11	15.0	15.0	2	10	3	19.0	16.7
0	5	4	11.2	10.3	1	0	14	45.1	48.8	1	5	7	52.3	56.8	1	11	5	16.1	17.8	2	4	12	21.6	21.5	2	10	4	5.8	9.4
0	5	5	45.3	51.8	1	0	18	28.9	26.7	1	5	8	22.2	24.9	2	0	3	59.0	69.5	2	4	13	14.5	13.4	2	10	5	9.7	8.5
0	5	6	21.4	18.1	1	0	19	8.2	7.0	1	5	9	37.7	43.8	2	0	4	49.2	55.7	2	4	14	26.5	29.0	2	10	6	10.0	10.8
0	5	7	30.2	33.8	1	0	20	16.4	15.2	1	5	10	23.8	25.8	2	0	5	14.0	12.2	2	4	15	20.3	29.2	2	10	7	10.2	11.3
0	5	8	22.0	24.1	1	0	21	5.6	5.6	1	5	11	24.4	24.8	2	0	6	110.4	125.3	2	4	16	19.5	16.9	2	10	8	12.3	13.1
0	5	9	28.6	30.9	1	0	22	11.2	10.5	1	5	12	22.8	23.8	2	0	7	42.1	40.6	2	4	17	13.8	13.1	2	10	10	12.3	11.6
0	5	11	37.0	36.5	1	0	24	19.7	15.9	1	5	13	35.9	37.9	2	0	8	44.8	40.5	2	4	18	9.3	11.0	2	11	2	9.5	8.3
0	5	12	9.3	9.0	1	0	26	6.3	3.3	1	5	14	5.7	6.5	2	0	9	25.1	21.1	2	4	19	9.1	10.4	2	11	3	15.5	16.1
0	5	14	12.9	13.0	1	1	2	21.4	20.9	1	5	15	20.5	20.2	2	0	10	48.0	53.4	2	4	20	15.8	14.8	2	11	3	6.5	5.8

TABLE 1.3 Cont.

H	K	L	|Fo|	|Fc|
5	9	11	7.0	6.7
5	9	12	7.4	6.7
5	10	0	9.3	9.4
5	10	2	9.8	9.7
5	10	4	11.6	11.3
5	10	5	7.9	7.2
5	10	6	16.9	16.8
5	10	7	7.8	8.2
5	10	8	11.0	11.7
5	10	9	7.2	7.2
6	0	3	38.4	35.4
6	0	4	49.6	42.4
6	0	5	65.8	53.2
6	0	6	21.4	18.6
6	0	7	25.4	26.1
6	0	8	18.3	17.4
6	0	9	23.6	25.0
6	0	10	37.7	37.2
6	0	11	49.5	48.0
6	0	12	10.8	8.1
6	0	13	6.5	6.0
6	0	14	22.3	19.0
6	0	15	16.4	13.9
6	0	16	25.5	24.7
6	0	17	27.2	28.8
6	0	18	11.4	10.9
6	0	20	10.0	9.0
6	0	21	12.4	11.7
6	0	22	18.7	17.4
6	0	23	12.2	11.4
6	1	0	78.0	64.1
6	1	1	21.5	20.3
6	1	2	23.7	18.9
6	1	3	16.2	16.1
6	1	4	71.8	61.7
6	1	5	24.5	27.2
6	1	6	40.6	44.0
6	1	7	28.9	28.7
6	1	8	15.8	14.8
6	1	9	18.2	16.6
6	1	10	26.8	27.7
6	1	11	26.7	23.4
6	1	12	36.1	33.0
6	1	13	7.6	6.6
6	1	14	9.5	9.9
6	1	15	18.7	19.3
6	1	16	30.3	29.4
6	1	17	12.2	10.0
6	1	18	13.9	15.1
6	1	19	14.6	15.7
6	1	20	13.5	13.7
6	1	21	9.4	8.7
6	1	22	11.7	9.6
6	2	0	44.4	37.5
6	2	1	70.9	66.0
6	2	2	20.9	22.9
6	2	3	18.6	17.3
6	2	4	23.3	22.7
6	2	5	60.2	61.2
6	2	6	25.5	24.2
6	2	7	23.7	25.6
6	2	8	23.5	21.8
6	2	10	32.3	31.3
6	2	11	28.3	28.5
6	2	12	22.4	20.8
6	2	13	13.9	15.2
6	2	14	17.3	17.4
6	2	15	23.8	24.8
6	2	16	14.0	13.9
6	2	17	16.1	16.3
6	2	19	5.4	5.5
6	2	20	9.0	7.3
6	2	21	10.8	10.1
6	2	22	6.9	7.1
6	3	0	24.8	25.9
6	3	1	7.7	6.6
6	3	2	21.6	19.2
6	3	3	36.6	37.0
6	3	4	24.4	27.1
6	3	5	20.9	22.9
6	3	6	37.1	36.9
6	3	7	13.1	12.8
6	3	8	9.0	8.2
6	3	9	13.7	13.6
6	3	10	26.3	27.3
6	3	11	15.1	16.3
6	3	12	29.0	28.9
6	3	13	10.5	10.8
6	3	14	9.0	9.5
6	3	15	21.8	21.3
6	3	16	18.5	17.2
6	3	18	6.7	7.9
6	3	20	13.5	13.5
6	3	21	7.9	6.7
6	3	22	8.7	9.3
6	3	23	6.0	6.9
6	4	0	53.0	46.6
6	4	1	30.6	32.9
6	4	2	24.0	23.5
6	4	3	17.0	16.5
6	4	4	33.1	34.0
6	4	5	38.3	39.2
6	4	6	32.5	33.5
6	4	7	22.2	26.5
6	4	8	26.6	30.3
6	4	9	7.6	6.7
6	4	10	7.7	7.1
6	4	11	24.7	26.5
6	4	12	11.3	11.1
6	4	13	20.2	22.7
6	4	14	12.2	13.3
6	4	15	17.1	18.2
6	4	17	12.2	13.9
6	4	18	10.4	12.1
6	4	19	6.0	6.6
6	4	20	5.6	5.4
6	4	21	10.5	11.9
6	4	22	7.9	8.3
6	5	0	50.4	42.1
6	5	1	37.9	33.7
6	5	2	17.5	16.8
6	5	3	28.7	28.9
6	5	4	22.6	19.6
6	5	5	17.3	19.6
6	5	6	10.8	10.4
6	5	7	18.2	22.9
6	5	8	7.9	8.2
6	5	9	19.9	22.7
6	5	10	10.6	10.1
6	5	11	24.0	26.0
6	5	12	16.2	17.8
6	5	14	9.7	10.0
6	5	15	10.3	11.2
6	5	16	16.4	18.4
6	5	18	8.3	7.8
6	6	0	17.2	16.5
6	6	1	14.2	11.6
6	6	2	23.4	22.1
6	6	3	24.8	23.9
6	6	4	17.8	15.4
6	6	5	31.0	31.6
6	6	6	14.5	16.2
6	6	7	20.2	20.0
6	6	9	20.7	22.0
6	6	10	14.5	14.6
6	6	11	18.8	20.7
6	6	12	12.5	13.2
6	6	13	7.7	7.7
6	6	14	11.8	14.8
6	6	15	17.6	18.3
6	6	16	6.8	7.6
6	7	0	10.7	9.7
6	7	1	11.4	11.3
6	7	2	9.1	8.9
6	7	3	15.7	16.2
6	7	4	20.2	20.2
6	7	5	24.9	24.0
6	7	6	13.9	14.9
6	7	7	16.6	19.2
6	7	8	10.4	11.2
6	7	9	15.6	17.3
6	7	10	10.1	10.0
6	7	11	7.5	8.5
6	7	12	5.1	5.9
6	7	13	12.9	15.4
6	7	15	13.7	14.2
6	7	16	10.2	9.4
6	7	17	10.6	10.3
6	8	0	16.4	16.8
6	8	1	17.7	19.6
6	8	2	15.4	16.0
6	8	3	19.1	18.4
6	8	4	14.7	14.6
6	8	5	15.0	15.0
6	8	6	13.9	14.5
6	8	7	9.6	9.2
6	8	8	8.7	7.4
6	8	9	14.7	12.3
6	8	10	14.5	12.5
6	8	11	11.0	10.7
6	8	12	13.5	13.7
6	8	13	5.6	5.8
6	8	14	11.9	11.0
6	8	15	11.9	11.4
6	9	0	21.3	18.5
6	9	1	19.6	17.1
6	9	2	18.7	17.3
6	9	3	15.3	13.9
6	9	4	11.6	10.8
6	9	5	12.6	12.5
6	9	6	9.2	9.8
6	9	7	14.8	16.0
6	9	8	4.9	5.1
6	9	9	15.9	16.6
6	9	11	11.6	12.5
6	9	12	9.8	10.4
6	10	2	10.3	10.6
6	10	3	5.0	5.4
6	10	4	5.2	5.6
6	10	5	6.9	7.1
6	10	6	9.6	9.8
7	0	0	23.3	22.3
7	0	7	37.5	37.2
7	0	8	5.8	4.8
7	0	9	49.5	46.6
7	0	11	11.8	10.6
7	0	12	10.0	9.8
7	0	13	36.0	36.4
7	0	14	7.5	4.9
7	0	15	33.8	34.6
7	0	17	13.1	14.0
7	0	18	7.4	7.7
7	0	19	21.3	20.2
7	0	20	7.9	9.1
7	0	23	7.7	7.7
7	1	3	23.4	25.1
7	1	4	32.0	33.4
7	1	5	9.0	9.1
7	1	6	9.2	9.3
7	1	7	21.7	20.4
7	1	8	29.0	27.8
7	1	9	7.4	6.7
7	1	10	8.3	7.6
7	1	11	6.2	5.3
7	1	12	30.0	25.3
7	1	13	9.3	8.5
7	1	14	9.5	7.6
7	1	15	14.6	14.0
7	1	17	8.2	8.4
7	1	18	9.3	7.9
7	1	19	9.9	9.6
7	1	20	17.0	15.0
7	2	0	32.1	33.6
7	2	1	22.7	27.2
7	2	2	24.0	29.2
7	2	3	45.1	54.0
7	2	4	9.1	8.8
7	2	5	22.1	22.9
7	2	6	19.6	17.4
7	2	7	45.1	44.6
7	2	8	27.9	26.9
7	2	9	48.3	47.2
7	2	10	7.5	6.5
7	2	11	10.0	9.8
7	2	13	35.1	31.9
7	2	15	9.6	7.4
7	2	17	13.7	14.0
7	2	18	8.5	9.2
7	2	19	16.8	17.1
7	2	22	6.1	6.9
7	2	23	5.9	6.3
7	3	0	4.3	3.2
7	3	1	20.6	19.4
7	3	2	24.9	25.4
7	3	3	18.3	20.5
7	3	4	25.5	25.9
7	3	5	25.1	25.2
7	3	6	29.7	32.2
7	3	7	21.6	20.5
7	3	8	46.4	45.7
7	3	9	32.3	31.6
7	3	10	26.1	24.8
7	3	11	31.2	30.6
7	3	12	30.9	28.3
7	3	13	24.0	22.8
7	3	14	26.6	25.4
7	3	15	9.6	9.0
7	3	16	4.7	5.0
7	3	17	10.2	11.9
7	3	18	19.4	19.1
7	3	19	6.5	6.8
7	3	20	10.4	9.8
7	3	21	7.6	8.7
7	3	22	5.0	4.9
7	4	0	5.7	5.8
7	4	1	26.0	21.8
7	4	2	13.9	13.7
7	4	3	33.3	33.1
7	4	4	11.5	11.2
7	4	5	19.0	19.2
7	4	7	18.2	16.7
7	4	8	27.2	26.9
7	4	9	30.9	31.8
7	4	10	7.5	8.4
7	4	11	14.8	14.0
7	4	12	14.0	14.9
7	4	13	29.8	29.3
7	4	14	13.5	14.5
7	4	15	8.1	9.1
7	4	16	9.6	10.5
7	4	17	8.1	8.2
7	4	18	13.0	15.0
7	4	19	5.5	8.7
7	5	0	15.9	16.2
7	5	1	25.9	24.8
7	5	2	36.0	31.6
7	5	3	16.5	13.5
7	5	4	17.2	16.2
7	5	5	16.3	16.2
7	5	6	19.3	20.5
7	5	7	26.4	30.5
7	5	9	18.6	18.5
7	5	10	20.4	23.6
7	5	11	19.5	23.1
7	5	12	10.6	11.3
7	5	14	11.6	11.8
7	5	15	10.3	11.6
7	5	17	5.8	8.5
7	5	18	8.5	10.1
7	5	19	7.6	7.3
7	5	20	5.5	5.4
7	5	21	10.5	11.1
7	5	22	6.9	6.8
7	6	1	27.3	20.6
7	6	3	23.5	23.1
7	6	4	19.5	17.7
7	6	5	21.5	22.9
7	6	6	18.7	16.3
7	6	7	16.3	17.5
7	6	9	13.4	13.7
7	6	10	15.2	14.8
7	6	11	9.8	10.0
7	6	12	10.5	10.9
7	6	13	4.4	5.2
7	6	14	6.6	7.0
7	6	18	7.4	7.9
7	6	19	8.4	8.8
7	7	1	23.6	21.2
7	7	2	25.2	23.8
7	7	3	8.9	8.0
7	7	4	28.9	28.9
7	7	5	15.9	17.6
7	7	6	12.3	11.0
7	7	7	15.6	16.1
7	7	8	24.3	24.3
7	7	9	4.4	4.7
7	7	10	7.5	7.2
7	7	11	10.2	10.8
7	7	12	8.4	9.5
7	7	13	8.8	8.4
7	7	14	12.1	11.2
7	7	15	8.4	8.1
7	8	0	14.8	14.8
7	8	1	11.9	10.3
7	8	2	17.6	16.6
7	8	3	12.9	11.2
7	8	4	8.6	7.8
7	8	5	6.6	6.7
7	8	6	19.6	18.5
7	8	7	9.5	9.6
7	8	8	9.1	9.6
7	8	9	6.5	6.7
7	8	10	8.4	7.7
7	8	11	9.5	8.4
7	8	12	9.0	7.9
7	8	13	6.9	5.9
7	9	1	17.9	14.6
7	9	2	7.5	6.5
7	9	3	9.3	9.7
7	9	5	16.5	14.9
7	9	7	14.4	12.1
7	9	8	10.8	9.5
7	9	9	20.6	22.2
7	9	10	31.7	29.0
7	9	11	12.7	11.6
7	9	12	30.2	30.6
8	0	0	30.4	29.3
8	0	11	7.9	7.3
8	0	12	14.9	14.5
8	0	13	30.6	27.3
8	0	15	6.3	6.5
8	0	16	21.1	14.5
8	0	17	5.5	6.7
8	0	19	10.8	11.1
8	0	21	12.4	13.5
8	1	1	10.7	9.6
8	1	2	28.9	36.3
8	1	3	7.0	7.5
8	1	5	37.5	38.5
8	1	6	9.1	8.0
8	1	7	12.9	11.2
8	1	9	9.6	10.2
8	1	10	33.2	37.5
8	1	11	7.8	7.1
8	1	12	29.2	27.3
8	1	13	5.1	4.3
8	1	14	6.3	6.7
8	1	15	10.3	10.1
8	1	16	20.0	20.8
8	1	18	9.5	9.4
8	1	20	9.6	9.5
8	1	22	9.0	10.4
8	2	0	5.2	5.0
8	2	1	25.9	30.8
8	2	2	22.9	27.4
8	2	3	10.4	9.9
8	2	5	35.9	37.6
8	2	6	32.0	30.5
8	2	7	21.3	20.2
8	2	8	7.7	7.0
8	2	9	13.0	12.8
8	2	10	17.3	16.5
8	2	11	20.7	19.5
8	2	12	6.3	6.0
8	2	13	15.1	13.3
8	2	14	9.7	9.9
8	2	15	16.2	14.0
8	2	17	14.1	14.1
8	2	21	6.8	7.7
8	3	0	46.5	46.8
8	3	1	12.5	11.3
8	3	2	19.6	20.5
8	3	3	22.8	24.9
8	3	4	40.8	43.3
8	3	5	23.5	23.5
8	3	6	38.9	31.4
8	3	7	14.7	15.9
8	3	8	15.7	14.2
8	3	9	16.4	15.3
8	3	10	18.3	16.2
8	3	11	7.3	6.9
8	3	12	14.6	15.3
8	3	13	6.3	4.7
8	3	14	10.3	10.0
8	3	15	5.0	6.0
8	3	16	13.3	15.0
8	3	20	8.3	9.7
8	4	1	32.7	29.8
8	4	2	21.7	23.5
8	4	3	30.4	28.2
8	4	4	10.7	9.4
8	4	5	28.5	28.7
8	4	6	10.5	10.6
8	4	7	12.8	13.0
8	4	8	18.0	20.7
8	4	9	16.7	16.8
8	4	10	12.7	11.1
8	4	11	26.7	29.9
8	4	12	8.9	9.4
8	4	13	7.2	6.6
8	4	14	10.5	10.9
8	4	15	10.7	10.9
8	4	16	10.4	10.2
8	5	0	37.2	34.1
8	5	2	26.0	20.4
8	5	5	14.1	14.0
8	5	6	17.1	16.7
8	5	7	7.3	7.1
8	5	8	9.0	8.6
8	5	9	17.5	19.2
8	5	11	10.7	12.0
8	5	12	14.0	13.7
8	5	13	9.6	10.4
8	5	16	15.7	16.4
8	5	18	8.0	8.0
8	6	1	15.5	12.5
8	6	2	9.0	8.2
8	6	3	8.2	8.0
8	6	4	18.3	20.1
8	6	5	23.0	22.2
8	6	6	10.9	11.8
8	6	7	10.8	9.5
8	6	8	10.1	10.5
8	6	9	13.5	14.6
8	6	10	10.3	9.9
8	6	11	16.6	16.7
8	6	13	6.1	6.3
8	6	14	13.1	12.5
8	6	15	12.7	13.7
8	6	16	9.1	9.6
8	6	17	9.5	10.4
8	7	0	15.3	14.4
8	7	1	11.6	11.8
8	7	2	9.3	9.2
8	7	4	6.9	6.8
8	7	5	14.9	13.0
8	7	6	12.6	11.3
8	7	7	11.9	10.4
8	7	8	5.6	4.8
8	7	9	10.8	12.0
8	7	10	15.6	15.4
8	7	11	8.1	7.6
8	7	12	10.7	9.2
8	7	13	13.4	12.9
8	7	14	11.0	10.5
8	7	15	8.1	8.9
8	8	0	8.1	6.6
8	8	1	11.9	12.0
8	8	2	19.3	17.9
8	8	4	11.9	9.1
8	8	5	15.6	15.7
8	8	6	11.4	11.4
8	8	8	14.2	13.4
8	8	9	5.8	7.5
8	8	10	7.8	6.6
8	8	11	11.1	11.3
8	9	0	9.2	8.0
8	9	1	3.9	7.7
8	9	3	12.9	12.8
8	9	4	10.3	9.6
8	9	5	7.5	7.9
8	9	6	6.5	7.2
8	9	8	49.4	49.4
8	9	9	8.1	8.9
8	9	10	30.7	27.4
8	9	11	17.8	15.7
8	9	12	5.2	5.2
8	9	13	23.6	24.0
8	9	14	21.7	21.0
8	9	15	13.7	11.5
8	9	16	13.1	13.4
8	9	17	6.5	6.6
8	9	18	13.1	13.4
8	9	19	6.5	6.6
8	9	21	32.6	30.2
8	10	0	5.6	6.2
8	10	2	19.6	24.9
8	10	3	14.2	15.6
8	10	4	17.6	19.5
8	10	5	17.2	17.9
8	10	6	9.8	9.5
8	10	7	15.1	14.5
8	10	8	26.2	26.6
8	10	9	6.0	4.4
8	10	10	7.2	6.8
8	10	11	9.7	8.0
8	10	12	16.2	14.4
8	10	13	10.6	9.2
9	1	14	17.8	16.5
9	1	15	5.1	3.5
9	1	16	6.1	5.4
9	1	18	15.0	12.5
9	1	20	9.2	10.4
9	2	0	15.9	15.2
9	2	1	22.2	26.2
9	2	2	19.0	21.9
9	2	3	30.1	34.5
9	2	4	13.1	11.4
9	2	5	12.3	12.1
9	2	6	5.8	5.1
9	2	7	39.2	40.6
9	2	8	12.0	8.2
9	2	9	38.5	37.0
9	2	10	3.7	3.2
9	2	11	16.2	15.7
9	2	12	7.5	7.3
9	2	13	19.3	18.0
9	2	14	6.4	4.9
9	2	15	8.0	7.1
9	2	16	6.9	6.9
9	2	17	5.6	7.0
9	2	18	6.0	5.3
9	2	19	13.9	15.2
9	3	0	7.0	6.9
9	3	1	5.4	4.3
9	3	2	28.6	26.5
9	3	3	12.6	13.3
9	3	4	25.0	25.9
9	3	5	10.7	11.1
9	3	7	17.1	16.1
9	3	8	23.6	23.8
9	3	9	11.7	11.3
9	3	10	9.1	9.3
9	3	11	14.5	13.5
9	3	12	12.3	13.8
9	3	13	7.3	7.1
9	3	14	17.1	17.9
9	3	17	10.5	11.0
9	3	18	8.2	8.6
9	4	0	12.7	12.9
9	4	1	18.3	16.8
9	4	2	12.8	10.6
9	4	3	22.0	20.3
9	4	4	8.1	6.8
9	4	5	12.6	13.7
9	4	6	8.2	8.8
9	4	7	17.4	17.4
9	4	8	7.5	6.7
9	4	9	13.5	12.6
9	4	10	9.1	9.3
9	4	11	7.4	7.2
9	4	12	8.1	8.0
9	4	13	16.8	21.7
9	4	15	9.6	10.6
9	4	16	7.9	8.4
9	4	17	8.1	8.6
9	5	2	21.7	17.6
9	5	3	10.6	8.6
9	5	4	16.3	15.6
9	5	5	24.8	24.8
9	5	6	12.9	12.0
9	5	8	28.1	29.4
9	5	9	12.6	12.3
9	5	10	10.1	11.9
9	5	11	11.0	11.8
9	5	12	12.1	13.4
9	5	14	9.1	9.7
9	5	15	10.1	10.0
9	6	0	17.3	14.9
9	6	1	15.6	13.5
9	6	3	21.4	20.1
9	6	4	12.6	11.7
9	6	5	12.6	11.3
9	6	6	14.7	13.5
9	6	7	15.3	14.7
9	6	8	4.9	4.1
9	6	9	12.6	14.0
9	6	10	5.6	5.6
9	6	11	6.2	7.5
9	6	12	5.1	3.8
9	6	13	10.1	10.4
9	7	0	8.9	7.6
9	7	1	14.3	10.8

TABLE 1.4

FRACTIONAL COORDINATES AND E.S.D.S.

Atom	x/a	y/b	z/c
Br	0.2221 ± 1	-0.7349 ± 1	0.0933 ± 0
O(1)	0.9873 ± 7	0.6098 ± 7	0.0627 ± 3
O(2)	1.0641 ± 6	0.4831 ± 8	0.2013 ± 4
O(3)	0.6211 ± 8	0.5419 ± 8	-0.0353 ± 3
O(4)	0.7172 ± 7	0.6575 ± 6	0.0390 ± 3
O(5)	0.7291 ± 8	0.0195 ± 6	0.1110 ± 4
O(6)	0.5385 ± 7	0.1120 ± 6	0.1219 ± 3
O(7)	0.5222 ± 9	-0.1117 ± 8	0.2003 ± 3
C(1)	0.7774 ± 8	0.6680 ± 7	0.0998 ± 3
C(2)	0.9032 ± 10	0.7186 ± 9	0.0894 ± 4
C(3)	1.0047 ± 9	0.6618 ± 9	0.1264 ± 4
C(4)	0.9788 ± 8	0.5468 ± 9	0.1745 ± 4
C(5)	0.8466 ± 8	0.5280 ± 8	0.1949 ± 3
C(6)	0.8229 ± 10	0.3921 ± 10	0.2357 ± 4
C(7)	0.8071 ± 10	0.2459 ± 9	0.2020 ± 4
C(8)	0.7003 ± 7	0.2650 ± 7	0.1539 ± 3

P . T . O .

TABLE 1.4 cont.

Atom	x/a	y/b	z/c
C(9)	0.7419 ± 6	0.3803 ± 6	0.1044 ± 3
C(10)	0.7531 ± 6	0.5307 ± 6	0.1403 ± 3
C(11)	0.6333 ± 7	0.4093 ± 7	0.0597 ± 3
C(12)	0.6554 ± 8	0.5380 ± 8	0.0180 ± 3
C(13)	0.8221 ± 10	0.6695 ± 11	0.2340 ± 5
C(14)	0.8513 ± 8	0.3279 ± 8	0.0672 ± 3
C(15)	0.6610 ± 9	0.1190 ± 7	0.1279 ± 4
C(16)	0.4904 ± 11	-0.0265 ± 8	0.0991 ± 4
C(17)	0.4794 ± 8	-0.1399 ± 8	0.1501 ± 3
C(18)	0.4190 ± 6	-0.2841 ± 7	0.1347 ± 3
C(19)	0.4150 ± 8	-0.3963 ± 8	0.1800 ± 3
C(20)	0.3570 ± 7	-0.5289 ± 8	0.1670 ± 3
C(21)	0.3021 ± 7	-0.5533 ± 7	0.1103 ± 3
C(22)	0.3044 ± 8	-0.4453 ± 8	0.0647 ± 4
C(23)	0.3636 ± 8	-0.3080 ± 8	0.0785 ± 3

TABLE 1.5

ORTHOGONALISED COORDINATES AND E.S.D.S.(Å)
REFERED TO THE CRYSTALLOGRAPHIC AXES

ATOM	X	Y	Z
Br	2.389 ± 1	-6.576 ± 1	2.034 ± 1
O(1)	10.618 ± 7	5.456 ± 6	1.366 ± 6
O(2)	11.445 ± 7	4.322 ± 7	4.387 ± 8
O(3)	6.680 ± 9	4.849 ± 7	-0.770 ± 6
O(4)	7.714 ± 8	5.883 ± 5	0.850 ± 6
O(5)	7.842 ± 8	0.174 ± 6	2.419 ± 9
O(6)	5.792 ± 7	1.002 ± 5	2.657 ± 7
O(7)	5.616 ± 10	-0.999 ± 7	4.365 ± 7
C(1)	8.361 ± 8	5.977 ± 6	2.175 ± 7
C(2)	9.714 ± 10	6.430 ± 8	1.948 ± 9
C(3)	10.806 ± 10	5.922 ± 8	2.753 ± 9
C(4)	10.527 ± 8	4.893 ± 8	3.803 ± 8
C(5)	9.105 ± 8	4.725 ± 7	4.246 ± 6
C(6)	8.851 ± 11	3.508 ± 9	5.135 ± 8
C(7)	8.680 ± 10	2.201 ± 8	4.401 ± 8
C(8)	7.532 ± 8	2.371 ± 6	3.353 ± 7

P . T . O .

TABLE 1.5 cont.

ATOM	X	Y	Z
C(9)	7.980 ± 7	3.402 ± 5	2.275 ± 6
C(10)	8.099 ± 7	4.749 ± 6	3.057 ± 7
C(11)	6.811 ± 8	3.662 ± 6	1.300 ± 7
C(12)	7.049 ± 9	4.814 ± 8	0.392 ± 7
C(13)	8.842 ± 11	5.990 ± 10	5.099 ± 10
C(14)	9.156 ± 9	2.934 ± 7	1.464 ± 7
C(15)	7.109 ± 10	1.065 ± 7	2.787 ± 8
C(16)	5.274 ± 12	-0.238 ± 7	2.159 ± 9
C(17)	5.156 ± 8	-1.251 ± 7	3.270 ± 7
C(18)	4.507 ± 7	-2.542 ± 7	2.934 ± 6
C(19)	4.463 ± 8	-3.547 ± 7	3.923 ± 7
C(20)	3.840 ± 8	-4.733 ± 7	3.638 ± 7
C(21)	3.249 ± 8	-4.951 ± 7	2.403 ± 7
C(22)	3.274 ± 8	-3.984 ± 7	1.409 ± 8
C(23)	3.910 ± 8	-2.756 ± 7	1.710 ± 7

TABLE 1.6

ASSUMED FRACTIONAL CO-ORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF THE NON-METHYL HYDROGEN ATOMS

Atom	x/a	y/b	z/c	Uiso
H(1)	0.733	0.754	0.128	0.04
H(2)	0.872	0.829	0.077	0.05
H(3)	1.079	0.716	0.153	0.05
H(10)	0.664	0.547	0.162	0.03
H(8)	0.616	0.305	0.175	0.04
H(61)	0.904	0.381	0.265	0.05
H(62)	0.737	0.414	0.261	0.05
H(111)	0.622	0.410	0.031	0.04
H(112)	0.551	0.434	0.086	0.04
H(71)	0.892	0.216	0.179	0.05
H(72)	0.783	0.158	0.234	0.05
H(161)	0.397	-0.006	0.080	0.06
H(162)	0.549	-0.068	0.063	0.06
H(19)	0.458	-0.378	0.225	0.04
H(20)	0.353	-0.617	0.201	0.04
H(22)	0.261	-0.466	0.021	0.04
H(23)	0.365	-0.219	0.045	0.04

TABLE 1.7

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.(in A^2)

ATOM	U11	U22	U33	2U23	2U31	2U12
Br	0.0547 6	0.0432 3	0.0586 4	-0.0163 6	0.0076 7	-0.0271 6
O(1)	0.0525 42	0.0582 33	0.0601 30	-0.0060 56	0.0230 53	-0.0129 60
O(2)	0.0402 41	0.0720 43	0.0933 48	-0.0086 76	-0.0297 64	0.0024 67
O(3)	0.0997 53	0.0573 34	0.0454 29	0.0181 53	-0.0383 63	0.0032 72
O(4)	0.0723 46	0.0333 24	0.0617 31	0.0289 45	-0.0210 66	-0.0127 57
O(5)	0.0551 50	0.0302 25	0.1443 69	-0.0221 64	0.0274 92	0.0013 58
O(6)	0.0435 42	0.0307 23	0.0900 40	-0.0098 52	-0.0151 65	-0.0070 47
O(7)	0.0869 62	0.0671 38	0.0586 31	-0.0076 60	-0.0509 69	-0.0677 84
C(1)	0.0420 48	0.0286 26	0.0488 35	0.0044 47	0.0055 69	-0.0055 55
C(2)	0.0565 63	0.0376 34	0.0683 47	-0.0033 73	0.0266 82	-0.0248 70
C(3)	0.0440 55	0.0453 38	0.0666 48	-0.0141 69	0.0170 74	-0.0268 72
C(4)	0.0275 45	0.0508 39	0.0522 39	-0.0276 66	-0.0003 59	0.0036 62
C(5)	0.0409 46	0.0410 34	0.0376 31	-0.0194 50	0.0089 55	0.0076 65
C(6)	0.0612 61	0.0572 45	0.0490 41	0.0163 72	-0.0095 73	-0.0298 79
C(7)	0.0558 52	0.0480 40	0.0563 40	0.0230 68	-0.0145 66	0.0058 75

P . T . O .

TABLE 1.7 cont.

ATOM	U11	U22	U33	2U23	2U31	2U12
C(8)	0.0268 40	0.0295 26	0.0553 34	0.0054 51	-0.0019 52	-0.0082 51
C(9)	0.0245 39	0.0215 22	0.0381 27	-0.0004 39	-0.0045 44	0.0022 40
C(10)	0.0308 40	0.0242 23	0.0467 31	-0.0035 44	0.0055 47	0.0000 45
C(11)	0.0240 43	0.0284 27	0.0477 32	0.0027 49	0.0019 51	0.0016 47
C(12)	0.0370 46	0.0492 36	0.0370 31	0.0136 53	-0.0085 58	-0.0025 68
C(13)	0.0707 64	0.0606 47	0.0650 56	-0.0561 86	0.0360 89	-0.0022 88
C(14)	0.0364 47	0.0325 31	0.0564 38	-0.0084 56	0.0141 65	0.0120 61
C(15)	0.0569 55	0.0232 27	0.0685 44	0.0177 55	0.0049 78	-0.0145 61
C(16)	0.0809 78	0.0287 32	0.0636 46	0.0126 64	-0.0347 95	-0.0191 77
C(17)	0.0413 47	0.0448 35	0.0452 36	-0.0045 57	-0.0061 58	-0.0143 62
C(18)	0.0234 38	0.0366 29	0.0424 30	0.0068 50	-0.0121 47	-0.0067 50
C(19)	0.0394 46	0.0430 35	0.0412 33	-0.0019 56	-0.0099 54	-0.0135 58
C(20)	0.0387 46	0.0476 34	0.0372 30	0.0115 53	0.0116 56	0.0016 62
C(21)	0.0297 44	0.0349 29	0.0463 32	-0.0147 47	-0.0064 50	-0.0281 52
C(22)	0.0488 50	0.0455 35	0.0414 33	-0.0003 56	-0.0292 59	-0.0095 65
C(23)	0.0386 46	0.0407 35	0.0427 34	0.0122 52	-0.0210 56	-0.0011 62

TABLE 1.8

PRINCIPAL VALUES AND DIRECTION COSINES OF VIBRATION TENSORS REFERRED TO THE CRYSTALLOGRAPHIC AXES

ATOM	U / Å^2	D1	D2	D3
Br	0.0333	0.4991	0.8439	0.1968
	0.0694	0.6204	-0.5065	0.5988
	0.0538	0.6050	-0.1768	-0.7763
O(1)	0.0714	0.5711	-0.4362	0.6954
	0.0433	-0.8193	-0.2506	0.5157
	0.0561	-0.0507	-0.8642	-0.5005
O(2)	0.0363	0.9677	-0.0022	0.2521
	0.0979	-0.2488	-0.1696	0.9536
	0.0712	0.0407	-0.9855	-0.1647
O(3)	0.1058	-0.9518	0.0256	0.3056
	0.0355	0.2726	-0.3861	0.8813
	0.0611	0.1406	0.9221	0.3605
O(4)	0.0272	-0.0432	-0.9263	0.3744
	0.0824	-0.7699	0.2697	0.5784
	0.0577	-0.6367	-0.2632	-0.7247
O(5)	0.1474	0.1456	-0.0921	0.9850
	0.0290	-0.0795	0.9914	0.1044
	0.0533	-0.9861	-0.0935	0.1370
O(6)	0.0915	-0.1499	-0.0708	0.9862
	0.0291	0.2891	0.9507	0.1123
	0.0436	-0.9455	0.3019	-0.1221
O(7)	0.1182	-0.8029	0.5089	0.3105
	0.0288	0.5852	0.5739	0.5728
	0.0656	0.1133	0.6416	-0.7586
C(1)	0.0277	-0.2112	-0.9689	0.1286
	0.0498	0.3123	0.0578	0.9482
	0.0419	-0.9262	0.2404	0.2904
C(2)	0.0787	0.5859	-0.2083	0.7832
	0.0309	-0.4872	-0.8628	0.1350
	0.0529	0.6476	-0.4607	-0.6069

P . T . O .

TABLE 1.8 cont.

ATOM	U (A^2)	D1	D2	D3
C(3)	0.0741	0.4068	-0.3910	0.8256
	0.0312	-0.7350	-0.6768	0.0417
	0.0506	0.5424	-0.6238	-0.5627
C(4)	0.0654	-0.0356	-0.6896	0.7233
	0.0273	-0.9927	0.1076	0.0537
	0.0378	-0.1149	-0.7161	-0.6885
C(5)	0.0270	-0.3878	0.5935	0.7053
	0.0491	-0.0073	-0.7671	0.6415
	0.0434	0.9217	0.2436	0.3018
C(6)	0.0771	-0.6979	0.6476	0.3057
	0.0421	-0.4202	-0.7160	0.5574
	0.0482	0.5799	0.2606	0.7719
C(7)	0.0375	0.3473	-0.7344	0.5831
	0.0664	-0.4265	0.4301	0.7957
	0.0562	-0.8351	-0.5251	-0.1639
C(8)	0.0556	-0.0483	0.1101	0.9927
	0.0238	-0.8049	-0.5928	0.0265
	0.0321	0.5914	-0.7978	0.1173
C(9)	0.0385	-0.1607	-0.0220	0.9868
	0.0211	0.3291	-0.9437	0.0325
	0.0245	0.9305	0.3300	0.1589
C(10)	0.0473	0.1640	-0.0745	0.9836
	0.0241	-0.0330	0.9962	0.0810
	0.0304	-0.9859	-0.0458	0.1609
C(11)	0.0478	0.0421	0.0710	0.9966
	0.0238	-0.9860	0.1640	0.0300
	0.0284	-0.1614	-0.9839	0.0769
C(12)	0.0528	-0.1860	0.8831	0.4307
	0.0317	0.5623	-0.2638	0.7838
	0.0388	0.8058	0.3879	-0.4475
C(13)	0.0311	-0.2987	0.6515	0.6973
	0.0985	0.4748	-0.5324	0.7008
	0.0667	0.8279	0.5404	-0.1503

P . T . O .

TABLE 1.8 cont.

ATOM	U (Å^2)	D1	D2	D3
C(14)	0.0588	0.2767	-0.0895	0.9568
	0.0262	-0.6131	0.7502	0.2475
	0.0403	-0.7400	-0.6551	0.1527
C(15)	0.0200	-0.2012	-0.9618	0.1856
	0.0703	0.0871	0.1711	0.9814
	0.0584	-0.9757	0.2136	0.0493
C(16)	0.0937	-0.8367	0.1734	0.5194
	0.0267	-0.1409	-0.9848	0.1018
	0.0529	0.5292	0.0120	0.8484
C(17)	0.0344	0.7440	0.5809	0.3301
	0.0504	-0.6225	0.7822	0.0266
	0.0465	-0.2427	-0.2253	0.9436
C(18)	0.0213	0.9562	0.1538	0.2492
	0.0461	-0.2913	0.4129	0.8629
	0.0350	0.0298	-0.8977	0.4396
C(19)	0.0319	0.7449	0.4934	0.4491
	0.0490	-0.6516	0.6825	0.3311
	0.0427	-0.1431	-0.5393	0.8299
C(20)	0.0311	-0.5736	-0.2451	0.7816
	0.0510	0.2732	0.8423	0.4647
	0.0413	-0.7722	0.4801	-0.4162
C(21)	0.0163	0.7290	0.6429	0.2351
	0.0509	0.2789	-0.5927	0.7556
	0.0437	0.6251	-0.4853	-0.6114
C(22)	0.0610	-0.7812	0.2332	0.5790
	0.0294	0.6206	0.1908	0.7605
	0.0452	0.0669	0.9535	-0.2938
C(23)	0.0534	-0.5433	0.3815	0.7478
	0.0288	0.6893	-0.3058	0.6568
	0.0397	0.4793	0.8723	-0.0968

TABLE 1.9

SOME SHORT INTERATOMIC DISTANCES (in Å)

Intramolecular distances (<2.5Å)

Atom A	Atom B	A-B	Atom A	Atom B	A-B
O(1)	C(1)	2.453	C(6)	C(13)	2.482
O(2)	C(3)	2.374	C(6)	C(8)	2.492
O(2)	C(5)	2.379	C(8)	C(10)	2.462
O(3)	O(4)	2.182	C(10)	C(11)	2.435
O(3)	C(11)	2.389	C(11)	C(14)	2.461
O(4)	C(2)	2.346	C(15)	C(16)	2.336
O(4)	C(11)	2.439	C(17)	C(19)	2.485
O(5)	O(6)	2.224	C(17)	C(23)	2.500
O(5)	O(8)	2.407	C(18)	C(20)	2.396
O(6)	C(8)	2.321	C(18)	C(22)	2.435
O(6)	C(17)	2.420	C(19)	C(21)	2.400
O(7)	C(16)	2.359	C(19)	C(23)	2.414
O(7)	C(18)	2.378	C(20)	C(22)	2.418
C(4)	C(13)	2.393	C(21)	C(23)	2.395

Intermolecular distances (<3.8Å)

Atom A	Atom B	E.P.*	Cell**	A-B
Br	O(3)	2	-1 -1 0	3.214
Br	O(2)	1	-1 -1 0	3.497
Br	C(12)	2	-1 -1 0	3.709

P . T . O .

TABLE 1.9 cont.

Atom A	Atom B	E.P.*	Cell**	A-B
Br	O(6)	1	0 -1 0	3.721
O(1)	C(22)	1	1 1 0	3.447
O(1)	O(3)	2	0 1 0	3.484
O(1)	C(16)	2	0 0 0	3.603
O(1)	C(23)	2	0 0 0	3.792
O(2)	C(20)	1	1 1 0	3.239
O(2)	C(21)	1	1 1 0	3.254
O(3)	C(2)	2	-1 1 0	3.387
O(3)	C(3)	2	-1 1 0	3.540
O(3)	C(23)	2	0 0 0	3.654
O(4)	C(23)	2	0 0 0	3.293
O(4)	C(22)	2	0 0 0	3.551
O(4)	O(5)	1	0 1 0	3.601
O(5)	C(2)	1	0 -1 0	3.313
O(5)	C(1)	1	0 -1 0	3.197
O(7)	C(20)	3	1 0 0	3.256
O(7)	C(19)	3	1 0 0	3.312
C(1)	C(17)	1	0 1 0	3.798
C(2)	C(23)	2	0 0 0	3.768
C(3)	C(22)	1	1 1 0	3.621
C(3)	C(21)	1	1 1 0	3.749

P . T . O .

TABLE 1.9 cont.

Atom A	Atom B	E.P.*	Cell**	A-B
C(7)	C(19)	3	1 0 0	3.734
C(10)	C(19)	1	0 1 0	3.794
C(11)	C(21)	1	0 1 0	3.744
C(11)	C(22)	1	0 1 0	3.770
C(12)	C(23)	1	0 1 0	3.672

* Integers under this column refer to the following equivalent positions

1) x , y , z ;

2) 1/2 + x , 1/2 - y , -z ;

3) - x , 1/2 + y , 1/2 - z .

** For any distance the triple set of integers given under this column indicate the unit-cell translation that must be added to the appropriate equivalent position to derive the co-ordinates of the atom under the column Atom B from those given in Table 1.4 .

TABLE 1.10

Deviations (in Å) of atoms from the mean planes through

a) C(1) to C(4) ;

b) O(1) , C(2) and C(3) ;

c) C(6) , C(7) , C(9) and C(10) ;

d) O(4) , C(1) , C(11) and C(12) ;

e) C(18) to C(23) ;

f) C(16) , C(17) , C(18) and O(7) .

Atom	(a)	(b)	(c)	(d)	(e)	(f)
Br	-	-	-	-	-0.012	-0.071
O(1)	1.234	0.000	-	-	-	-
O(2)	0.159	-	-	-	-	-
O(3)	-	-	-	0.109	-	-
O(4)	0.860	-	-	-0.026	-	-
O(5)	-	-	-	-	2.050	2.041
O(6)	-	-	-	-	-0.107	-0.151
O(7)	-	-	-	-	-0.105	0.004
C(1)	-0.004	-1.203	-	0.012	-	-
C(2)	0.007	0.000	-	1.035	-	-
C(3)	-0.007	0.000	-	-	-	-
C(4)	0.003	-1.270	2.092	-	-	-
C(5)	-0.370	-	0.595	0.432	-	-

P . T . O .

TABLE 1.10 cont.

Atom	(a)	(b)	(c)	(d)	(e)	(f)
C(6)	-	-	0.015	-	-	-
C(7)	-	-	-0.015	-	-	-
C(8)	-	-	-0.794	0.413	-	-
C(9)	-	-	0.015	0.734	-	-
C(10)	0.267	-	-0.015	-0.003	-	-
C(11)	-	-	-	-0.011	-	-
C(12)	-	-	-	0.025	-	-
C(13)	-0.440	-	-	-	-	-
C(14)	-	-	-	1.210	-	-
C(15)	-	-	-1.114	-	0.961	0.953
C(16)	-	-	-	-	0.079	0.003
C(17)	-	-	-	-	-0.030	-0.010
C(18)	-	-	-	-	0.005	0.003
C(19)	-	-	-	-	-0.001	0.085
C(20)	-	-	-	-	0.000	-
C(21)	-	-	-	-	-0.002	-
C(22)	-	-	-	-	0.005	-
C(23)	-	-	-	-	-0.007	-0.111

3.1.7 Discussion

The x-ray crystal structure analysis of the p-bromophenacyl derivative of palmarin has confirmed the β-opoxide configuration (See Fig. 1.2 and Fig. 1.5), as predicted by Overton, Weir and Wylie (1966); hence the unknown configuration of epoxides in the group of Colombo root bitter principles having composition $C_{20}H_{22}O_7$ (jateorin, chasmanthin and palmarin) was decided.

The presence of the β-epoxide in palmarin has caused the intramolecular overcrowding which is accommodated in the structure in an interesting way causing the conformational distortions (Fig. 1.5) which, from a study of the Dreiding model, might appear unreasonable. From an examination of the Dreiding model Overton, Weir and Wylie (1966) have further suggested that due to interaction between the epoxide oxygen O(1) and the methyl carbon C(14) although the ring "A" (Fig. 1.4a) would be slightly distorted, there would be the usual chair formation of the cyclohexane ring "B" and half chair formation of δ-lactone ring C. The extent of deviations from these theoretical predictions can be evaluated from the following discussion. The distance between

the epoxide oxygen O(1) and methyl carbon C(14), 2.92 ± 0.01 Å, is shorter than the sum of the two corresponding normal van der Waals' radii (3.3 Å). This indicates that the molecule might be under some strain. The mean plane through the atoms C(1) to C(4), calculated by the method of Schomaker et al. (1959), has the equation

$$0.1402\,X - 0.7302\,Y - 0.6687\,Z + 4.6435 = 0 \qquad (3)$$

where X, Y and Z (in Å) are the orthogonal co-ordinates with reference to the crystallographic axes. The root mean square (r.m.s.) distance of the four atoms from the mean plane is 0.006 Å. The appropriate χ^2 test (See Sec. I, 1.8.5) shows that these atoms may be considered as coplanar. Atoms C(5) and C(10) of the same ring (A) are displaced through -0.370 and 0.267 Å respectively (Table 1.10a) towards opposite sides of the plane.

The dihedral angle between the plane and the mean plane through the epoxide ring [O(1), C(2) and C(3)] having equation

$$0.5864\,X + 0.7407\,Y - 0.3279\,Z - 9.8203 = 0 \qquad (4)$$

is 104°.

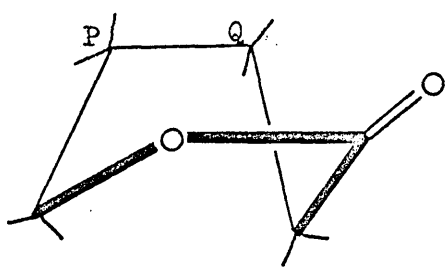
The equation of the mean plane through the four atoms [C(6), C(7), C(9) and C(10)] of the cyclohexane ring "B" is

$$0.9541\,X + 0.0633\,Y - 0.2928\,Z - 7.1476 = 0 \qquad (5)$$

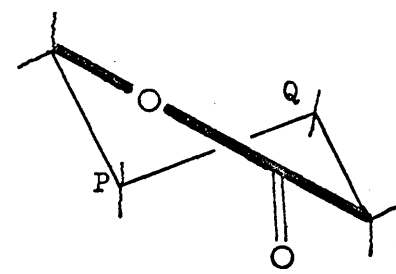
Displacement of the atoms C(5) and C(8) from this plane are 0.595 and -0.794 Å respectively [Table 1.10 (c)] whereas in an undisturbed cyclohexane ring these two deviations are expected to be equal. This distoriton is almost certainly caused by the interaction between the epoxide oxygen O(1) and the methyl carbon C(14). The methyl carbon C(13), attached to the carbon atom C(5), might also be partially responsible for this slight deformation of the cyclohexane ring (B).

Cheung, Overton and Sim (1965) have reported two types of confomrations for δ-lactone;

(i) the half-boat conformation (VII), in which carbon atoms P and Q of the lactone ring are displaced to the same side of the plane containing the lactone group C-C(=O)-O-C



VII



VIII

(ii) the half-chair conformation (VIII), where carbon atoms P and Q are on opposite sides of the lactone plane. The conformation of the δ-lactone in palmarin (VI) was suggested by Overton, Weir and Wylie (1966) as of the type (VIII).

The best plane through the atoms of the lactone group [O(4), C(1), C(11) and C(12)] has the equation

$$0.8377\ X - 0.4184\ Y - 0.3509\ Z - 3.7284 = 0 \qquad (6)$$

The r.m.s. distance of these atoms from the mean plane is 0.02 Å. The appropriate χ^2 test shows that the lactone group may be considered as planar. Displacements of 0.734 and -0.003 Å of the carbon atoms C(9) and C(10) from this plane [Table 1.10 (d)] indicate that C(10) may be regarded as coplanar with the lactone plane whereas the deviation of C(9) out of the plane is significant. This confirms that the conformation of δ-lactone in palmarin is neither of the type (VII) nor of (VIII).

The equation of the best plane through the atoms [C(18) to C(23)] of the benzene ring "D" is

$$0.8619\ X - 0.3711\ Y - 0.3456\ Z - 3.8083 = 0 \qquad (7)$$

The r.m.s. deviation (0.004 Å) of the atoms of the ring and their individual displacements [Table 1.10 (e)] show that the benzene ring is planar. The deviation of the Br atom(-0.012Å) out of this plane is not significant.

The mean plane through the atoms of the carbonyl group [C(16), C(17), O(7)] and aromatic carbon C(18) has the equation

$$0.8828\,X - 0.3848\,Y - 0.2695\,Z - 4.1622 = 0 \qquad (8)$$

The angle of twist between this plane and the mean plane through atoms of the benzene ring is 4.6°. This small rotation is probably due to the intermolecular packing effect caused by the special arrangement of the molecules (see Fig. 1.3).

The carbon-bromine bond length of 1.874 ± 0.007 Å is similar to that of 1.870 ± 0.010 Å in propargyl 2-bromo-3-nitro-benzoate (Calabrese, McPhail and Sim, 1967) and is not far from the normal accepted value of 1.85 ± 0.01 Å (Int. Tables, Vol. III, 1962). The individual C-C bond in the benzene ring (Fig. 1.4) is not significantly different from the mean value of 1.394 ± 0.010 Å and is similar to the standard value, 1.395 ± 0.003 Å (Int. Tables, Vol. III, 1962). The average of the C-C single bonds in the slightly

distorted cyclohexane ring, B, (1.549 ± 0.011 Å), agrees quite well with the accepted value of 1.540 Å (Tables of international distances, 1958, 1965). The mean value of the carbon-carbon bonds adjacent to the C-O double bond is 1.493 Å and is what is expected in such a case. The average of the C-O distances in the epoxide ring 1.463 ± 0.011 Å is near to 1.47 ± 0.01 Å, quoted in Int. Tables, Vol. III, (1962). The carbon-carbon distance in the epoxide part [C(2) - C(3)], 1.449 ± 0.013 Å is comparable with the corresponding value of 1.46 ± 0.01 Å in 3β-acetoxy-7α, 11α-dibromolanostane-8α, 9α-epoxide (Fawcett and Trotter, 1966). All the carbon-oxygen double bonds are individually similar to their mean value of 1.218 Å (Fig. 1.4a). This may be compared with that of 1.223 Å in the case of 2-chloro-1, 8-phthaloyl naphthalene (Sec. II, Chapt. 4). No other valency bonds, shown in Fig. 1.4a, differ significantly ($< 3\sigma$) from normal values expected in similar situations.

Intermolecular separations C(1) ...O(5) (3.20 Å), Br...O(3) (3.21 Å) and Br...C(12) (3.71 Å) appear to be slightly shorter than the corresponding sumsof the normal van der Waals' radii (3.3, 3.3 and 3.9 Å respectively). No other intermolecular distance is significantly shorter than the appropriate van der Waals contact (Table 1.3).

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APPENDICES

APPENDIX A

The unsuccessful attempt to solve the structures of three solvated heavy atom containing crystals of phorbol is an example of the difficulties faced with the solvated derivative.

Phorbol, a natural product having molecular formula $C_{20}H_{28}O_6$ is isolated from Croton oil, a vesiccant substance containing co-carcinogens which are phorbol esterified fatty acids. On the basis of the spectroscopic evidence various structures had been assigned to it. Several aspects of all of these were unsatisfactory. Professor Crombie and his collaborators prepared heavy atom solvate derivatives of phorbol for us. 1:3-Dibromobenzene, bromothiophen and iodobenzene formed the solvated crystals of the compounds "Phorbol$_2$Solvate$_1$". The crystals of the three solvated derivatives were isomorphous. The systematic absences indicated space group C2, C2/m and Cm but since the material was optically active the space group could only be C2 which would inevitably lead to a pseudo symmetry problem in a heavy atom phased electron density distribution. We had expected to overcome this by use of multiple isomorphous replacement as Cheung and Sim (1964) had done for aflatoxin G_1.

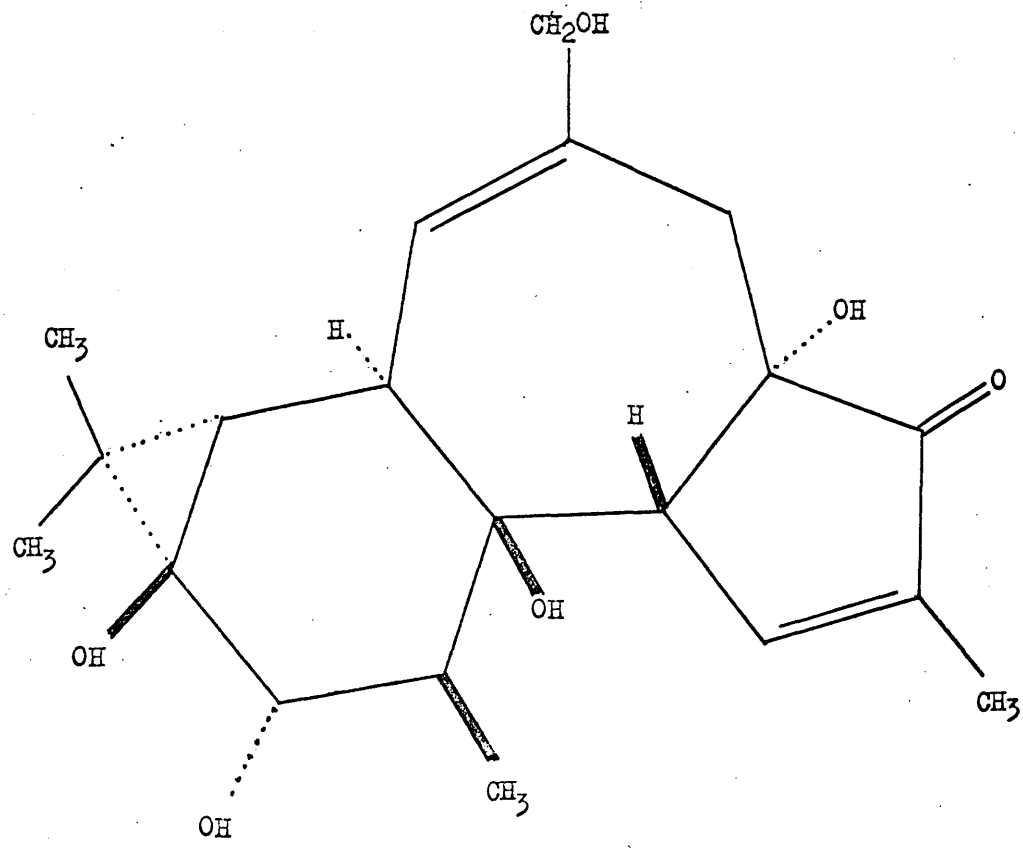
In collaboration with Drs. G. Birnbaum and J.G. Sime three dimensional intensity data of dibromobenzene and bromothiophane solvated phorbol were collected on the linear diffractometer. For the iodobenzene solvated derivative photographic methods were employed. The relevant crystal data are given below

Crystal data	Dibromobenzene solvate	Bromothiophen solvate	Iodobenzene solvate
a	26.420 Å	26.626 Å	26.83 Å
b	15.121 Å	15.035 Å	14.90 Å
c	14.654 Å	14.624 Å	14.86 Å
β	91.5°	91.4°	92.3°
Space group	C2	C2	C2
D_m	1.28 gm/cc.	1.29 gm/cc.	1.32 gm/cc.
D_c (Z = 4)	1.38 gm/cc.	1.30 gm/cc.	1.32 gm/cc.

It was found to be impossible to interpret the Harker section of each of the structures; no clearly defined maxima for the heavy atom vectors were obtained. Further investigation by Professor Crombie and his co-workers showed that the derivatives

were losing solvent molecules slowly and the Harker sections indicated that what was left was probably disordered within the phorbol cage.

The structure of phorbol has recently been determined using a 5-bromofuroate derivative which had a molecule of chloroform as a solvate. These crystals were unstable at room temperature and hence the three dimensional x-ray data were collected at -160°C. by Pettersen et al. (1967) using the cooling device described in Appendix B. The structure for phorbol is found to be



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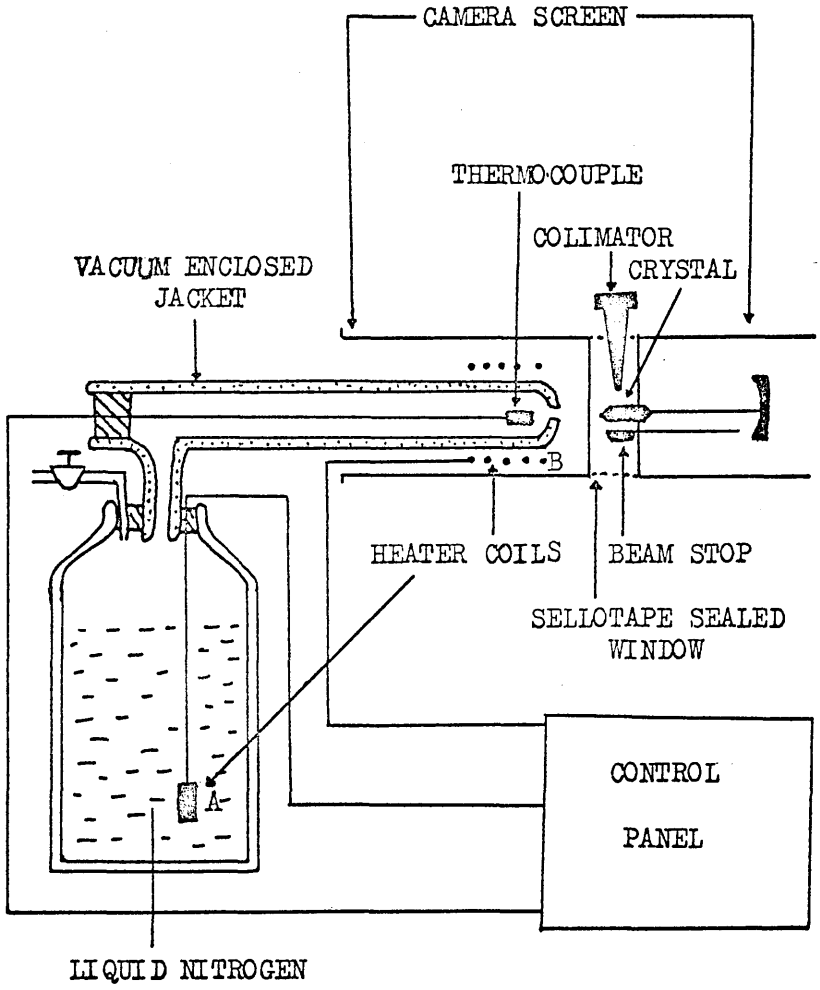
APPENDIX B

To collect the photographic data at low temperature a cooling system was developed for the Nonius Weissenberg camera using liquid nitrogen as the cooling source; Nonius provided various thermal jackets and thermocouples for leading cold gas to a crystal on the camera and nothing else. The arrangement which was finally found to be most suitable for our needs was to boil liquid nitrogen and pass the cold gas over the crystal.

A 25 litre Dewar flask is used as "boiler" and a 50 watt heater (A) is immersed in the liquid nitrogen in the "boiler". The power to the heater is controlled by a "variac control unit". The general outline of the arrangement is shown in the diagram. To avoid the formation of ice over the crystal a small heater coil (B) warms the gas after it has cooled the crystal – but this was not enough to keep the film and cassette from being covered with ice. Eventually the arrangement found most suitable, was to enclose the whole camera in a polythene tent. Initially, the moisture of the enclosed atmosphere in the tent is absorbed by silica gel. As the cooling is started the positive pressure of



The sectional diagram showing the arrangement for collecting the photographic data in the cold nitrogen atmosphere (the diagram is not true to the scale).

the dry nitrogen atmosphere prevents moist air from entering into the tent through small leakages. Either Ni foil or sellotape can be used to seal the slit in between the two cylindrical screens of the camera allowing the diffracted x-rays to pass but not the cold gas.

To save the crystal from being knocked or cracked in the jet of cold nitrogen gas, a coating of acetone collodian over the crystal mounted on the goniometer head is found helpful.

With this arrangement, some 3000 intensity data of an iron-thiocarbonyl complex of cyclopentabutadiene were collected. Due to the shortage of time, the structure analysis has been temporarily postponed.